The DOCUMENT examiner had trouble with forensic discrimination between types of toner using a single analysis method. In our study, seven samples of toner removed from laser printers of various and same brands of different models will be analysed using more than one method as Fourier transform infrared (FT-IR), Raman spectroscopy, X-ray fluorescence (XRF) and X-ray diffraction (XRD) to distinguish between different toner samples and applying all analysis data for forensic evidence. Results of FT-IR analysis show that all toner samples of HP brand had the same polymeric resin. Raman spectroscopy used to differentiate between toner samples had the same polymeric resin in FT-IR analysis by comparing their Raman spectrum. Toner samples of HP 2300 and HP 4700 printers were indistinguishable by using results of FT-IR and Raman spectroscopy, therefore, more elemental analysis will be required. XRF used to differentiate between indistinguishable toner samples of HP 2300 and HP 4700 printers by FT-IR and Raman spectroscopy. Also for all toner samples, results of XRF shown that iron, silicon, copper, calcium, and ruthenium were the major percent elements present in toner. The results of XRD show that here are common compounds (phases) between the analyzed toner samples and the composition for major elements present were oxides.

**Keywords:** Toner analysis, Laser printer, Raman spectroscopy, FT-IR, XRF, XRD, Forensic discrimination.

**Introduction**

Various documents can be produced by digital printing methods such as dye sublimation, laser, and inkjet printers. In line with the technical progress, using different types of digital printing is growing because of its presence and getting it from the sale of printers and computer accessories stores which led to the spread in offices, libraries, educational centers and homes[1-3]. So, using of laser printing has spread dramatically in modern life because it is easier, faster, cheaper and higher quality, therefore, the printout of laser printers heavily used create different documents as letters, wills and contracts which exposed permanently to criminal operations such as exploit written signature from the hands of its owner, changing one or more pages of the contract exploited exist the signature on the last page only and blank paper contains signature only with very few printed words near signature[4-7]. Accordingly, ink of laser printers is toner which differs in composition from ordinary handwriting ink. Toner consists of main components as polymeric resin, iron oxide, colored pigments as carbon black, other than these principal components, toner contain other additives as waxes and amorphous SiO₂. The most common resin types used in toner include styrene-acrylates, polystyrenes, and epoxies which in the last step are melted under high temperature and pressure to fuse on paper and then transfer into a solid state to fix on the printout at normal temperature. Iron oxide in toner transfer by electrostatic attraction to create the image on paper from a negative image on a drum during the printing process. The toner composition varies depending on manufacturers and according to the change in polymeric resin.
and/or other additives from brand to brand[8, 9]. It has been found that many single analysis methods can be used for investigating toner, such as: thin-layer chromatography (TLC), (FT-IR), Pyrolysis–gas chromatography–mass spectrometry, Raman spectroscopy, laser desorption mass spectrometry, desorption electrospray ionization mass spectrometry, calorimetry, Capillary electrophoresis, Direct analysis in real time-Mass spectrometry, Laser induced breakdown spectroscopy, Also combined methods are used as pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), Laser ablation–inductively/plasma-Mass spectrometry and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX)[9-11]. And, the most of earlier manuscripts depending on analysis of organic compounds present in toner as a polymeric resin which may be similar in different types of toner and regardless other inorganic compounds as elements which may differ and benefit for discrimination between them [11].

In our study, we use a mixture of chemical and elemental methods to differentiate between the samples of the toner. Chemical analysis methods as FT-IR and Raman spectroscopy are used to identify the polymeric component present in toner samples to differentiate and classified them into more than one group. Elemental analysis methods as XRF and XRD are applied to know that the major elements are present in toner samples and examined the phase purities of major elements to discriminate them according to the observed data. The results obtained applied to determine whether the printout of laser printer has been subjected to fraud or not and come from the same source and the toner has the same chemical composition or not.

**Experimental**

**Specimen preparation**

Seven samples of printer toner listed in Table 1 are analyzed by FT-IR, Raman, XRF and XRD. For analyzing by Raman spectroscopy toner samples printed from each printer listed in by printing a text (font size 14, font type simplified Arabic) on A4 copy paper format, uncoated and white 80 g/m² (Pioneer, Portugal) while the other methods analyzed the toner removed directly from the cartridge of printer of various and same brands of different models, five of them were taken from the original toner cartridges and two were taken from toner cartridges refilled [12-14].

**TABLE 1. Specifications of the used samples.**

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Brand</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hp LaserJet</td>
<td>2300dn</td>
</tr>
<tr>
<td>2</td>
<td>Hp LaserJet</td>
<td>P1005</td>
</tr>
<tr>
<td>3</td>
<td>Hp LaserJet</td>
<td>P1005</td>
</tr>
<tr>
<td>4</td>
<td>Hp colour LaserJet</td>
<td>4700</td>
</tr>
<tr>
<td>5</td>
<td>LEXMARK</td>
<td>E350d</td>
</tr>
<tr>
<td>6</td>
<td>EPSON aculaser</td>
<td>M2000</td>
</tr>
<tr>
<td>7</td>
<td>Nashuatec</td>
<td>SPC410dn</td>
</tr>
</tbody>
</table>

**Analysis Methods of Toner**

**Fourier transform infrared (FT-IR)**

All toner samples analyzed by Fourier transform infrared (FT-IR) spectrum were recorded on ATI Mattson Genesis series (KBr disc method) apparatus, Model 960 M009 series (USA). The FT-IR spectrum was obtained in the transmittance format (%T) at 8 cm⁻¹ resolution with 75 scans in the range of 400–4000 cm⁻¹ [15,16].

**Raman spectroscopy**

Raman spectroscopy applied in our work was SENTERRA (Bruker, USA). Spectroscopic analysis Preliminary measurements conducted on printout documents to find the best excitation wavelength for the analysis. All results applied at excited wavelength 532 nm. The use of 532 nm excitation wavelength to record Raman spectrum could help the discrimination ability in this case [17,18].
**X-ray fluorescence (XRF)**

The elemental content of toner samples is determined by energy dispersive XRF spectrometry. Results performed on an Oxford ED 2000 X-ray fluorescence spectrometer with a silver cathode; helium used as the inert gas [12,15].

**X-ray diffraction (XRD)**

Identification of elemental compounds present in toner samples is conducted by X-ray diffraction analysis. The X-ray diffraction patterns are obtained using PANalytical X’Pert PRO MultiPurpose Diffractometer (MPD). Diffraction results can take place by exposing powder samples to Cu-Kα X-ray radiation, which has a characteristic wavelength (λ) of 1.5418 Å. X-rays formed by a Cu anode of power 40 kV and power of current 40 mA.

**Results and Discussions**

**Fourier transform infrared (FT-IR)**

From the FT-IR spectrum, all toner samples divided into (3) groups (I, II, III) which present in Table 2 based on polymeric resin structure.

### TABLE 2. The groups (I, II and III) of toner samples.

<table>
<thead>
<tr>
<th>Group number</th>
<th>Number of samples</th>
<th>Position of characteristic peaks (cm⁻¹)</th>
<th>Band indication</th>
<th>Polymer resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1, 2, 3, 4</td>
<td>700, 766 and (2927, 2857, 1453)</td>
<td>polystyrene</td>
<td>polystyrene/acrylate</td>
</tr>
<tr>
<td>II</td>
<td>5, 7</td>
<td>833 and 1513</td>
<td>Bisphenol A</td>
<td>epoxy</td>
</tr>
<tr>
<td>III</td>
<td>6</td>
<td>730, 1275</td>
<td>terephthalate</td>
<td>polyester/terephthalate</td>
</tr>
</tbody>
</table>

With respect to group (I) in Fig.1, the bands at 700 and 760 cm⁻¹ present in the spectrum of all samples of this group show the same place as bands originating from polystyrene, that also show absorption bands at 3059, 3026 cm⁻¹ due to the stretching vibrations of hydrogen in mono-substituted aromatic rings. Narrow bands at 1183 and 997 cm⁻¹ are associated with aliphatic acrylic esters, while bands at 2920, 2850 and 1452 cm⁻¹ arising from aliphatic –CH₂– groups of the polystyrene chain.

![Fig. 1. The FT-IR spectrum of toner samples of group (I).](attachment:image.png)
In group (II), the bands at 830 and 1510 cm\(^{-1}\) present in toner spectrum due to existing of bisphenol A as in Fig.2. The same bands can be observed in the spectrum of epoxy resins produced by this compound. Also, spectrum of the two toner samples in group (II) shows a band at 1250 cm\(^{-1}\) due to aromatic ethers.

Differences between a spectrum of the same group having the same polymeric material as groups (I and II) in Fig. 1 and 2 are due to the existence of different co-monomer concentrations and other additives present in toner.

Bands at 730 and 1271 cm\(^{-1}\) present in the spectrum of sample relating to a group (III) indicates the presence of paint resins such as terephthalate as in Fig. 3 [2,12].

**Discrimination of toner samples into three groups (I, II and III) can be arises from their spectrum in Fig.4.**

As can be seen in Fig.5, polystyrene/acrylate is the major polymer resin group with presence of 57% of all analyzed toner, followed by epoxy resin in 28%. The third major group is polyester/terephthalate present in 14% of all samples [15].

**Raman spectroscopy**

It was observed that from the results of FT-IR samples (1,2,3 and 4) located in group (I) and samples (5 and 7) located in group (II) are indistinguishable by FT-IR technique. Therefore, we need to apply another technique to help us to distinguish between the toner samples in the same group and confirm the results obtained by FT-IR analysis.

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**Fig. 2. The FT-IR spectrum of toner samples of group (II).**

**Fig. 3. The FT-IR spectrum of toner sample of group (III).**

*Egypt. J. Chem. 61*, No.1 (2018)*
Raman spectroscopy using for analysis of three toner samples (1, 3 and 4) present in the same group (I) to distinguish between them. Also, Raman spectroscopy used in analysis of sample (5) chosen from group (II) and sample (6) chosen from group (III) to know if Raman spectroscopy as a nondestructive method give the same results and can be distinguishable between toner samples of different groups as FT-IR destructive method or not.

The classification of toner samples based on Raman spectroscopy depends on three main factors, the presence or absence of peaks, peak place, and the relative intensities of the sharp peaks observed. Based on the above factors, two samples considered as different if there is at least one significant difference between Raman bands for two spectrums. If there is not enough variation, two samples classified into the same group and considered as the same.

It was observed that the toner samples (1 and 4) give the same bands at 132, 1330 and 1540 cm⁻¹ as shown in Fig. 6, so they are indistinguishable either by FT-IR or Raman spectroscopy techniques.

In the case of sample (3) Raman spectrum show four main bands at 85, 117, 205 and 252 cm⁻¹ as shown in Fig. 7 therefore, Raman spectrum easily differentiate between samples (1 and 3) or between samples (3 and 4) which is found in the same group of FT-IR technique.
Fig. 6. Raman spectrum of toner samples (1 and 4).

Fig. 7. Raman spectrum of toner sample (3).

Fig. 8. Raman spectrum of toner sample (5).

Fig. 9. Raman spectrum of toner sample (6).

Fig. 10. Raman spectrum of toner sample (3).

With respect to sample (5) Raman spectrum consists of three main bands at 86, 118 and 175 cm\(^{-1}\) as shown in Fig. 8.

In sample (6) Raman spectrum shows two large bands at 1233 and 2597 cm\(^{-1}\) as shown in Fig. 9.

A comparison of Raman spectrum for five toner samples (1, 3, 4, 5 and 6) classified them into four groups listed in Table 3 and illustrated in Fig. 10.


It was clear from Fig. 10 that samples of groups A, B, C, and D are quite different in their pattern as well as peak position and peak intensity. The presence of characteristic peaks at 132, 1290 and 1530 cm\(^{-1}\) in A; peaks at 86, 120, 200 and 258 cm\(^{-1}\) in B; peaks at 90, 123 and 180 cm\(^{-1}\) in C, and peaks at 1235 and 2065 cm\(^{-1}\) in D, distinguished them as different groups. The difference of the characteristic spectrum between B and C samples was narrow; both have peaked at 90, 120, 200 cm\(^{-1}\) but their relative intensities were different.
and in the group B present band at 258 cm\(^{-1}\) while in group C not present.

The above Raman results of the two toner samples confirmed the results obtained from FT-IR where samples (5 and 6) present in two different groups. But about the three toner samples (1, 4 and 3) of the same brand which present in the same group from results of FT-IR present in Raman spectrum in two different groups one of them contain samples (1 and 4) and the other contains (3), therefore the use of Raman as more analysis method is the distinction between sample (1 and 3) and between (4 and 3)\[18,19\].

\textit{X-ray fluorescence (XRF)}

Raman spectroscopic analysis can differentiate between samples (1 and 3) and between samples (3 and 4) which are in the same group in FT-IR spectrum but still a complementary process which cannot distinguish between the two samples (1 and 4) therefore, we need to more analysis process. So, XRF is another method used for the analysis of toner to detect elemental composition and discriminate between the two samples (1 and 4) of the same group in both Raman and FT-IR techniques.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Raman spectrum of toner sample (5).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Raman spectrum of toner sample (6).}
\end{figure}

\begin{table}[h]
\centering
\caption{Four groups of toner samples according to Raman spectrum.}
\begin{tabular}{lll}
\hline
Groups & Samples & Peaks (cm\(^{-1}\)) \\
\hline
A & 1, 4 & 132, 1330 and 1540 \\
B & 3 & 85, 117, 205 and 252 \\
C & 5 & 86, 118 and 175 \\
D & 6 & 1233 and 2597 \\
\hline
\end{tabular}
\end{table}
TABLE 4. XRF of two toner samples (1 and 4) of group (I)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Ru</th>
<th>Zn</th>
<th>Si</th>
<th>Re</th>
<th>Cr</th>
<th>Mn</th>
<th>Rb</th>
<th>Ni</th>
<th>P</th>
<th>K</th>
<th>Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>98</td>
<td>0.1</td>
<td>0.3</td>
<td>0.3</td>
<td>0.8</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.9</td>
<td>6.3</td>
<td>1.6</td>
<td>6</td>
<td>0.2</td>
<td>75</td>
<td>0.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.6</td>
<td>5.2</td>
<td>0.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>

TABLE 5. XRF of five toner samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Ru</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>Zn</th>
<th>Re</th>
<th>Ti</th>
<th>Ni</th>
<th>V</th>
<th>P</th>
<th>Sn</th>
<th>Rb</th>
<th>Sr</th>
<th>K</th>
<th>Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>98</td>
<td>0.1</td>
<td>0.3</td>
<td>0.3</td>
<td>0.8</td>
<td>0.1</td>
<td>0.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>96</td>
<td>0.1</td>
<td>0.1</td>
<td>1.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.9</td>
<td>6.3</td>
<td>1.6</td>
<td>6</td>
<td>--</td>
<td>75</td>
<td>0.2</td>
<td>0.3</td>
<td>--</td>
<td>0.6</td>
<td>5.2</td>
<td>--</td>
<td>0.8</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>79</td>
<td>0.2</td>
<td>2.4</td>
<td>0.1</td>
<td>0.5</td>
<td>13</td>
<td>0.6</td>
<td>0.1</td>
<td>1.5</td>
<td>0.1</td>
<td>0.6</td>
<td>0.8</td>
<td>0.1</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>96</td>
<td>0.1</td>
<td>0.3</td>
<td>0.1</td>
<td>0.5</td>
<td>0.6</td>
<td>--</td>
<td>--</td>
<td>2.1</td>
<td>0.1</td>
<td>0.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 10. Raman spectrum of toner samples no (1, 3, 4, 5 and 6).
By analyzing XRF data contained in Table 4Cr, Mn and Rb elements are present in sample (1) while disappeared in sample (4) also, we found that Ni, P, K and Sc elements are present in sample (4) and disappeared in sample (1), the elements Fe, Si, Ca, Cu, Zn, Ru, Re are present in both samples (1 and 4).

The above XRF results help us to distinguish between the two toner samples (1 and 4) which we can not discriminate between them using both Raman and FT-IR techniques.

So, the application of XRF procedure applying on five toner samples to know the major elements present in each sample, also to distinguish between the toner samples from their elemental composition.

The quantitative analysis of data listed in Table 5 show that iron, silicon, copper, calcium and ruthenium are the major elements percent present in toner because the first and the second used as a charge control and flow agents respectively, and these elements used as a guide for identifying the possible compounds present in the X-ray diffraction pattern of these toner samples[15,20].

**X-ray diffraction (XRD)**

A complementary technique is used to discriminate the phase purities of the major elements present in toner samples analyzed by X-ray fluorescence (XRF) examined by X-ray diffraction (XRD).

There are some characteristic peaks known from literature to be important in predicting the structure of toner samples by X-ray diffraction analysis. Moreover by careful analysis of these peaks as shown in Fig.11, one can have a good estimation about the relative percentage of the aliphatic and aromatic parts (amorphous phase) in the molecular structure of the toner samples which have 2θ range of (10-18°) corresponding to interplanar spacing (8.83-4.92Å) approximately. This broad hump in the background patterns of these samples attributed to organic material, where the main constituent of toner is polymer resin; styrene acrylate, polyester, and epoxies as mentioned before. This broad hump in the XRD patterns is especially pronounced, for toner powder samples (4 and 6) [21].

Also from Fig.11, the shift towards it is observed that higher 2θ there are some peaks arise from the substitute of heteroatoms. This was verified by XRF as in Table 4. Each pattern matched will with the standard patterns (JCPDS) to know the metal compounds present in all samples as in Table 6 and the forms of these phases are oxide compounds.

**TABLE 6. The obtained phases for different samples**

<table>
<thead>
<tr>
<th>phases</th>
<th>samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite Fe$_2$O$_4$</td>
<td>1,3,5,6</td>
</tr>
<tr>
<td>Silicon oxide SiO$_2$</td>
<td>1,3,4,5,6</td>
</tr>
<tr>
<td>Manganese Aluminum Oxide Mn$_2$AlO$_4$</td>
<td>1,3,6</td>
</tr>
<tr>
<td>Tin oxide SnO$_2$</td>
<td>3,5,6</td>
</tr>
<tr>
<td>Calcium oxide CaO$_2$</td>
<td>3,4,5</td>
</tr>
<tr>
<td>Titanium oxide TiO$_2$</td>
<td>5,6</td>
</tr>
<tr>
<td>Phosphate Oxide P$_2$O$_5$</td>
<td>4</td>
</tr>
<tr>
<td>Silicon Phosphate Oxide</td>
<td>4</td>
</tr>
<tr>
<td>SiP$_2$O$_7$</td>
<td></td>
</tr>
<tr>
<td>Ruthenium oxide RuO$_2$</td>
<td>3</td>
</tr>
<tr>
<td>Zinc iron oxide ZnFe$_2$O$_4$</td>
<td>1</td>
</tr>
<tr>
<td>Hematite Fe$_3$O$_4$</td>
<td>4</td>
</tr>
</tbody>
</table>

*Egypt. J. Chem. 61, No.1(2018)*
The common phases listed in Table 7, which show that, exist magnetite Fe$_3$O$_4$ and SiO$_2$ as a major oxide compounds in all toner samples except sample (4) which has hematite Fe$_2$O$_3$, beside small amount of metal oxides as TiO$_2$, CaO, Mn$_2$AlO$_4$, and SnO$_2$ are present in the constituent of toner.

**Conclusions**

The article proved that application of a series of analysis methods to arrive at the correct and last distinction between the different types of toner. The results of FT-IR classified all toner.
samples into three different groups depending on the polymeric resin present in samples.

Raman spectroscopy confirms some results of FT-IR and classified the toner samples into four groups.

The elemental analysis by XRF is distinguished between two toner samples which not discriminate using both Raman and FT-IR techniques and determined the major elements present in toner samples.

The results of XRD show that the phase purities of major elements present in toner samples determined by XRF. In general, Raman spectroscopy, XRF and XRD are complementary methods to FT-IR analysis giving good discrimination between all toner samples.

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