A paper reporting the use of Raman Spectroscopy in fire debris analysis is presented. Five polymer based samples, namely carpet (polypropylene), nylon stockings (nylon), foam packaging (polystyrene), CD cases (polystyrene) and DVD cases (polypropylene) were burnt with each one of the following ignitable liquids: petrol, diesel, kerosene and ethanol. Raman shifts were obtained and, in some cases, peaks were identified to correspond to pyrolysis products in the form of alkanes, aromatic or polyaromatic compounds. All pyrolysis peaks were used to produce a Principal Component Analysis (PCA) of the burned samples with the different ignitable liquids. The change in the Raman spectra made it possible to identify some of the pyrolysis products produced in the combustion and also to identify the different plastic materials in fire debris, even when different fuels have been used and the chemical and structural identity of the plastic has been altered in the fire.

Keywords: Fire debris; Raman Spectroscopy; Pyrolysis Products; Principal Component Analysis; Chemometrics; Forensic Science
1. Introduction

Investigation of fire and arson cases necessitates the analysis of smoke and fire debris, which involves the examination of samples to identify possible ignitable liquids, materials and the pyrolysis products produced during the combustion. The main challenge in analysing samples from a fire or arson scene is that as the event progresses and the burning continues, the evidence is lost due to combustion and thermal degradation [1]. Materials are altered and, in many cases, lose their characteristic properties and structural integrity making it difficult to identify them. Samples of burned materials need to be taken from the fire scene promptly to ensure as little contamination and loss of volatiles as possible.

In the analysis of fire debris and the search for ignitable liquid residues, chromatographic techniques have been favoured by fire investigators for the identification and confirmation of ignitable liquids and pyrolysis products [2]. Gas Chromatographs coupled to different detectors such as FID [3] and the most versatile MS [4] or MS-MS [5] have been widely used whereas liquid chromatographs fitted to UV-VIS [6] detectors are less frequent. Spectroscopic techniques based on the use of near or middle infrared spectra are scarce in the analysis of fire debris and they are focused in the analysis of the pyrolysis products found in the decomposition of materials such as plastics [7,8], wood [9] or paper [10]. This overwhelming use of chromatographic techniques versus the spectroscopic ones is mainly due to the fact that a more detailed description of the different components found in fire debris or pyrolysis samples can be obtained with the former. This is unavoidable and necessary when specific compounds need to be detected and/or quantified in the sample. This information is of little or no use when identification of the materials involved in the
fire is needed. Identification of the different materials involved in a fire is of paramount importance for reconstruction of fire or accident scenes. Fire or accident investigators need to be able to obtain a clear picture of what was the situation and the materials present prior to the event. In the case of aeroplane crashes the aircraft needs to be literally reconstructed piece by piece. If the aircraft has been severely damaged by fire, the identification and location of the different materials can be difficult and takes time. In other forensic cases presence of foreign materials in a fire scene can be of relevance to the case to indicate the intentionality of the event.

In these cases, spectroscopic techniques can be very useful tools for chemical profiling of pyrolysis products and fire debris. Multivariate analysis can also be of help in processing the vast amount of information obtained from a fire scene.

Raman spectroscopy is widely used in the analysis of plastics [11] and has been previously used for the analysis of pyrolysis products in polymer films using Surface Enhanced Resonance Raman Scattering (SERRS) [12] and the analysis of decomposition products of polymers [13] in materials science.

All the enormous potential of the use of Raman spectroscopy for fire analysis is still unveiled. Other advantages of Raman are its portability, fast and inexpensive analyses and reasonable acquisition costs.

The aim of this research is the analysis of burnt plastic debris using Raman spectroscopy assisted with multivariate analysis. The main plastics of interest are polypropylene (PP), nylon (polyamide) and polystyrene (PS). These plastics occur in many household items such as CD and DVD cases, carpets, textiles and furniture. Thus suggesting that in the event of a domestic fire, these materials are highly likely to be involved; therefore their analysis would be of much use to the both the fire scene investigators and forensic scientists. When analysed, raw materials have a
characteristic spectrum or ‘band fingerprint’ which will change during the burning process due to pyrolysis of the chemical compounds present in the material and also maybe due to presence of accelerant residues in the fire debris. The use of ignitable liquids may also change the spectra because of differences in calorific power of the fuels, obtaining different pyrolysis products as a consequence of this. By studying the change in the Raman spectra it may be possible to determine the nature of the sample and identify different plastic materials in fire debris, even when different fuels have been used. There is little information on the identification of plastic materials obtained from fire scenes. To the best of our knowledge this is the first time Raman spectroscopy is used in the analysis of fire debris for identification of plastic materials burned with different ignitable liquids. The unique combination of Raman spectroscopy together with the use of chemometrics allowed the identification of these materials, even after having been burned. The study of the Raman behaviour of different hydrocarbons and aromatic compounds obtained as pyrolysis products is also scarce in the literature and focused in environmental applications [14].

2. Materials and methods

2.1 Materials

Five polymer based samples, namely carpet (polypropylene), nylon stockings (nylon), foam packaging (polystyrene), CD cases (polystyrene) and DVD cases (polypropylene) were burned alone, in air and then with each of four ignitable liquids (petrol, diesel, kerosene and ethanol). Samples were purchased in the local stores as well as the ignitable liquids. Undecane, dodecane, tridecane, tetradecane and pentadecane were purchased from Sigma (St Louis, MO, US). Benzene and benzene
derivatives, namely butyl benzene and dimethyl benzene, and phenanthrene and pyrene were also purchased from Sigma.

2.2 Instruments

A Foram 685-2 Raman Spectral Comparator (Foster and Freeman, Evesham, UK) fitted with a CCD detector was used for analysis of the sample materials. A diode laser with a wavelength of 685 nm was used to excite the sample and the operating laser power was set up at 4.5 mW (100%). Ramskan 2 version 1.1.0.2 software (Foster and Freeman) was used for data analysis. Before use it was calibrated using a standard in the form of a 100% polystyrene bead. After successful calibration, analyses were performed from 200 to 2000 cm\(^{-1}\) spectral range with a spectral resolution of 8 cm\(^{-1}\) with variable integration times depending on the background fluorescence. As an average the integration time was five seconds and the final spectrum was obtained as an average of three replicates from the same spot in the debris sample.

Temperature measurements were obtained using a Raytemp 8 infrared thermometer from Electronic Temperature Instrument Ltd (Worthing, UK).

2.3 Methodology

All of the samples were cut into six squares of approximately 5cm by 5cm in size. The different materials were analysed using Raman microscopy in its original, unburned state. Following this, the material was placed in an aluminium can, ignited and burned in air with the different ignitable liquids of this study: petrol, diesel, kerosene and ethanol; 5mL of the chosen ignitable liquid were added in each case, as a pool on non-porous materials and absorbed into the material in the case of porous ones. The length of the burning process was timed and recorded and depended on the different materials and fuels used. For the analysis, the materials were only burned for a
maximum of 5 minutes to standardise the burning process with the different ignitable liquids (when considerable charring was observed and the ignitable liquid had completely burned out) and extinguished by oxygen starvation. After burning, the samples were left in the metal can to cool then placed in a labelled and sealed nylon bag until analysis.

Principal Component Analyses (PCA) were performed using Tanagra software [15] developed in the University Of Lyon (France). Peaks found in table I were used as input variables for the PCA for the different materials under study. These peaks were obtained as averages of different burning experiments. For each piece of material 5 points with similar degree of charring were tested.

3. Results and discussion

3.1 Analysis of raw and standard materials

Plastics are combustible materials derived from petrol and they present similar pyrolysis products when they burn. This implies that, once burned, some of these plastics will present similarities in their Raman spectra with some common bands, making their identification sometimes rather difficult. The three type of plastics presented in this study, namely polystyrene (PS), polypropylene (PP) and nylon (Ny), share some vibrational modes coming from the carbon framework in the range of 1443-1475 cm\(^{-1}\), but differ in the presence of amide groups (for Ny) (1267 cm\(^{-1}\)) and benzene groups (for PS) (998 cm\(^{-1}\)). These functional groups greatly help to identify them and define their Raman spectra in the raw material.

Figure 1 shows the main Raman spectra obtained for all these materials prior to burning them. This information will greatly assist in comparisons made with burnt samples to identify which bands have been lost or gained. Figure 2 shows the Raman
shifts obtained for different middle-chain-size alkanes with chain length ranging from 
C_{11} to C_{14}. The main Raman bands observed for this group of compounds are: 1430 
cm^{-1}, 1324 cm^{-1}, 1139 cm^{-1}, 1088 cm^{-1} and 900 cm^{-1} presenting in general an increase 
of the peak intensity with increasing chain length for most peaks. This behaviour has 
been previously reported in the literature in the case of alkanes [16] related to bands 
close to 1440 cm^{-1}. Some of these vibrational modes can be found in PP when Figures 
1c and 1d are analysed, but not in PS or Ny, supporting this idea of a vibrational mode 
associated to carbon long chains. These bands will disappear after the burning process 
helping us to interpret the type of alkane generated.

The main characteristic peak for benzene derivatives obtained in our analyses can be 
found at 998 cm^{-1}, which can be also obtained in the corresponding samples from PS 
foam and the CD case (1005 cm^{-1} and 976 cm^{-1}, respectively). The difference between 
these two values can be explained by the vibrational orientation and the state of the 
sample. Benzene derivatives standards used in our study were all in liquid state, which 
implies random orientation similar to that found in PS foam. To check this point, a 
sample of a PS reference material was used as PS is frequently used in Raman 
spectroscopy as a standard to calibrate and monitor the response of the instrument. 
From this test a peak corresponding to the aromatic vibration at 982 cm^{-1} was 
obtained, in line with the response observed for the PS CD case. This confirmed that 
there was a drift in the Raman signal obtained for this peak in PS foam due to 
orientation and physical state and confirmed the aromatic identity of the peak 
observed in this region. This strong/medium signal has also been previously reported 
in the literature [17,18] at 1000 cm^{-1} and 992 cm^{-1}, respectively.

Finally The Raman shifts obtained from nylon where compared with those reported in 
the literature for amide vibrations. Stuart [19] used the values to monitor how nylon
was affected by temperature. The conclusion of this study indicated that bands corresponding to amide III would decrease the intensity with increasing temperature. The nylon sample used in our study presents this band at 1267 cm$^{-1}$, allowing us to identify the amide III group present in the polymer, but was not present in the burned sample indicating that the amide group was either destroyed in the process or the intensity considerably reduced to a point in which was undetectable.

3.2. Analysis of burnt samples

After burning the samples, following the process described under materials and methods section, a characteristic high fluorescence background was found for all the samples. The bands obtained for the fire debris of plastics are in general quite weak, which is certainly a consequence of the fluorescence background observed.

Figure 3.a and 3.b show typical Raman spectra obtained from a sample of a burnt CD case made of polystyrene using petrol and diesel respectively. It can be observed in a direct way the presence/absence of bands depending on the fuel used even when the material burned is the same. Table I summarises all the peaks found for the different fuels used and for all the materials in this research. The most common peaks found for all the samples are those around 440-455 cm$^{-1}$, 485-500 cm$^{-1}$ and 550-565 cm$^{-1}$. This information will be of little value in order to cluster the different samples burned under different conditions when performing the multivariate analysis using principal component analysis (PCA), but it can offer a first clue about the nature of some of the pyrolysis products obtained. Based on the data obtained from the literature [17], in the region 400 to 600 cm$^{-1}$ we can identify medium intensity broad bands associated to alkane vibrational modes. According to Stauffer [20], common pyrolysis products of the combustion of PP are alkanes, alkenes and alkadienes following random scission.
These would be in line with the experimental evidence obtained for this plastic in our study, but also suggests that alkanes will be a common and major pyrolysis product for most of the plastics burned with the different fuels. These alkanes would be the result of fragmentation in the polymer structure. However, based on the results obtained from our analysis of linear chain alkanes in figure 2, we have to rule out their presence as none of the characteristic bands obtained for the latter were found in the fire debris analysed for all the polymers under study. This may indicate the presence of branched carbon chains. This assumption can be supported by the fact that branched carbon alkanes bands have been previously reported in the range 460-500 cm\(^{-1}\) (s-m) and 650-760 cm\(^{-1}\) (s), if attached to aromatic rings or alkene groups [16], which is our case.

The second most common peak found in table 1 are Raman shifts around 1490-1500 cm\(^{-1}\) consistent with the presence of aromatic rings, according to the literature [18]. Based on the experimental bands obtained from benzene and benzene derivatives, these would not be fairly abundant in the fire debris samples as a pyrolysis product and, only in some cases for the combustion of PS, a peak in the region of 990 cm\(^{-1}\) typical of benzene can be found. This would suggest that the main pyrolysis products of plastic combustion are alkanes and, in our samples, the presence of aromatic rings should be associated to heavier compounds such as poly aromatic rings, much less volatile than benzene.

Other peaks can also be interpreted using the scarce Raman information given in the literature for pyrolysis products. Thus, peaks found around 747 cm\(^{-1}\) in many of our fire debris samples can be associated, according to Patnaik [16], to alkane vibrations. Patnaik also identified peaks in the range 1029-1082 cm\(^{-1}\) as indicative of aromatic compounds, especially substitution reactions occurring in poly benzene rings.
Wavenumbers around 1646 cm\(^{-1}\) were also associated to poly aromatic hydrocarbons (PAH) according to our experimental work (see Figure 4). Some PAH, such as phenanthrene, pyrene or anthracene, presented bands around 1622-1648 cm\(^{-1}\). The experiments performed on these PAHs can indicate that the region around 1600 cm\(^{-1}\) and 1650 cm\(^{-1}\) correspond to polyaromatic vibrations of fused aromatic rings. The band at 1646 cm\(^{-1}\) can be found in PS CD burned with all the ignitable liquids used in this study (considering the shift due to the different chemical environment and orientation). Fire debris obtained when PS foam was burned was scarce, as the material was almost disintegrated during the burning process. Only in one case, when burned with ethanol, a band at 995 cm\(^{-1}\) associated to a benzene ring could be indentified. It is known that charred material due to its carbonaceous nature can help to retain volatile organic compounds (VOC). If little material is left after combustion, charred samples can hardly retain any of these compounds which could explain the absence of bands and presence of bands associated to alkanes (maximum polymer destruction → shorter monomer chain size found).

In table I we can observe a higher abundance of peaks for those samples burned with petrol in the case of PS CD when compared to the rest of the samples burned with other ignitable liquids. This fact can be associated to a higher number of pyrolysis products as a consequence of a more efficient combustion process. Experimental temperature data obtained from the different experiments supported this. As an example, the average burning temperature reached when PS CD was burned with petrol was 395 C compared to 301 C obtained for PP carpet under the same conditions. The more complex structure of polystyrene together with a higher combustion temperature, obtained during the burning process, would explain the appearance of pyrolysis products observed.
3.3 Chemometric analysis

The main aim of the work presented here is to establish whether Raman spectra recorded after combustion of plastics with different ignitable liquids present pyrolysis patterns informative enough to cluster these materials together, even after their structural and chemical integrity has been seriously damaged.

To answer this question the information obtained from the different burning experiments (not averaged peaks) with the different plastic materials was used to produce different score plots in PCA. The results of the multivariate analysis allowed us to classify the different plastics for the different ignitable liquids used in the experiments as can be seen in Figure 5. Figure 5a shows the clustering obtained with the different plastic when burned with petrol. In this analysis, the PS CD case shows a clear separation from the rest of the other plastics, which also clustered in different groups. As shown on the figure, PC2 shows the most discriminatory power. The percentage of variance obtained in this case was PC1=41% and PC2=26%. Figure 5b shows the results obtained in the case of burning the samples with kerosene. In this case PC2 is also the main discriminating axis, being PC1=43% and PC2=17%. The clusters can still be defined although there is some degree of overlapping between them. This is also the case for the samples burned with ethanol (Figure 5c). There is a clear cluster for PS CD case, with the rest of the clusters also showing some degree of overlapping. The variance obtained was PC1=39% and PC2=24%. Finally, the results obtained with diesel (Figure 4d) also showed a clustering pattern, with a cluster for nylon clearly defined. In this case PC1 and PC2 have almost the same statistical weight in the variance and the values obtained were PC1=33% and PC2=32%. The samples were also burned without any type of fuel to establish whether the presence
of the ignitable liquid could affect the obtained results (Figure 5e). It can be observed that only in the case of nylon and polystyrene from the CD case there is some degree of differentiation between the fire debris obtained with the different samples. In the rest of the cases there is a high degree of overlapping between the different samples (indicated by the numeral). It can also be seen that in these cases the identification of samples would be very difficult. The results for the variation in the PCA was PC1=38% and PC2=20%. Other combinations using the different PCs obtained in the analyses were tried and PCAs based on PC1 and PC2 resulted to produce the best discriminative plots.

The best results were clearly obtained for plastics burned with petrol, which supports the hypothesis that a much richer pyrolysis pattern, as that obtained for petrol, helped to establish chemical differences between the plastics after being burned. Kerosene also showed a higher abundance of bands associated to pyrolysis products and the score plots obtained in PCA also showed better clustering than for the remaining ignitable liquids. In all cases, differences in the pyrolysis patterns were good enough to separate the different samples into groups. This differentiation cannot be attributed to the presence of remaining bands from the original material. This can be easily demonstrated by, for example, comparing the original spectra obtained in the case of PS CD (Figure 1.a) with those obtained after the material had been burned with petrol (Figure 3.a) or diesel (Figure 3.b). This is the case for all samples burned with all the different ignitable liquids.

The results obtained in this research can open an opportunity to further investigate the use of Raman spectroscopy in fire investigations. There are still many questions that remain unanswered and further research is needed. Some areas for future improvements imply the use of silver or gold colloids to quench the fluorescence in...
order to obtain much more information on the different compounds present in the
debris by using SERS. Sensitivity can also be improved and more bands from
pyrolysis products might be detected, thus improving the chances for a much better
and finer clustering using PCA analysis. Another factor to explain the differences
observed in the clustering patterns of polymers is related to the use of fire retardants.
By law, polymers used in everyday and industrial products need to incorporate them
in their composition to improve their resistance to fire. This will certainly have an
impact in the way they burn and in the pyrolysis products obtained. This is not
necessarily a problem as they will also incorporate differences that may help to
discriminate between polymeric materials with the same chemical composition. These
fire retardants can explain the differences observed in our study, but more research in
this area is also needed. In our study it was decided to use real samples rather than
standards of polymeric substances trying to obtain a more realistic picture and present
a real possibility of using Raman to fire investigators and forensic scientists.

4. Conclusions

The different polymers under study (Polystyrene, polypropylene and nylon) in their
different forms (CD and DVD cases, foam, carpet) could be discriminated even after a
burning process that radically modified their physical and chemical structure. Use of
Principal Component Analysis of the Raman spectra obtained demonstrated that the
different materials could be clustered even if different fuels (petrol, kerosene, ethanol
and diesel) have been used to start the fire. Different pyrolysis products were
identified for each material and ignitable liquid used and the differences were
significant enough to obtain the observed discrimination. This study could greatly
help towards the identification of materials chemically and physically modified by
fires during fire or accident scene reconstructions.
5. Acknowledgements

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6. Literature


[last accessed: 23/12/09].


7. Captions

7.1 Table captions

Table I. Summary of the main bands observed when burning different materials with the accelerants under study. The figures show the average of the peaks found for the different samples (a minimum of 3 and a maximum of 8)

7.2 Figure captions

Figure 1. Raman spectra of (A) Polystyrene CD case, (B) Polystyrene PS foam, (C) Polypropylene carpet, (D) polypropylene DVD case and (E) nylon from stockings.

Figure 2. Raman shifts obtained for different alkanes: (a) tetradecane, (b) tridecane, (c) dodecane and (d) undecane.

Figure 3. Raman spectra of burned polystyrene samples from a CD case with (a) petrol (inset: zoomed area of the range 2200 to 900 cm\(^{-1}\)) and (b) diesel.

Figure 4. Raman spectra of (a) phenanthrene, (b) pyrene and (c) anthracene
Figure 5. PCA analysis of the Raman spectra of plastics burned with (a) petrol, (b) kerosene, (c) ethanol and (d) diesel (e) burned with no fuel added. A numeral appearing in some of the graphs indicates the number of elements in that location as a result of a very similar spectrum. Symbols represent: ● PP carpet, ▲ Nylon, □ PS foam, + PS CD case, X PP DVD case.
Figure 1a

Figure 1b
Figure 1c

Figure 1d
Figure 1e
Figure 2

Intensity (A.U.)

Wavenumber (cm\(^{-1}\))
Figure 3a

3a zoom
Figure 3b
Figure 4
Figure 5a
Figure 5b
Figure 5c
Figure 5d
Figure 5e
Table I. Summary of the main bands observed when burning different materials with the accelerants under study. The figures show the average of the peaks found for the different samples (a minimum of 3 and a maximum of 8)

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