

1 **This draft version was published in**
2 **Journal of Analytical and Applied Pyrolysis 91 (2011) 210–218**

3

4 **Fire debris analysis by Raman Spectroscopy and chemometrics**

5 J. González-Rodríguez^{1*}, N. Sissons¹, S. Robinson²

6 ¹ School of Natural and Applied Sciences, University of Lincoln, Brayford Pool,
7 Lincoln, LN6 7TS, UK. Tel: +44(0)1522886878, fax: +44(0)1522886791, e-mail:
8 jgonzalezrodriguez@lincoln.ac.uk.

9 ² North Kesteven School, Moor Lane, North Hykeham, Lincoln, LN6 9AG, UK.

10 Telephone: +44(0)1522 881010, Fax: +44(0)1522 881452

11 *Corresponding author

12

13 **Abstract**

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

26

27 **Keywords:** Fire debris; Raman Spectroscopy; Pyrolysis Products; Principal
28 Component Analysis; Chemometrics; Forensic Science

29

1 **1. Introduction**

2

3 Investigation of fire and arson cases necessitates the analysis of smoke and fire debris,
4 which involves the examination of samples to identify possible ignitable liquids,
5 materials and the pyrolysis products produced during the combustion.

6 The main challenge in analysing samples from a fire or arson scene is that as the event
7 progresses and the burning continues, the evidence is lost due to combustion and
8 thermal degradation [1]. Materials are altered and, in many cases, lose their
9 characteristic properties and structural integrity making it difficult to identify them.

10 Samples of burned materials need to be taken from the fire scene promptly to ensure
11 as little contamination and loss of volatiles as possible.

12 In the analysis of fire debris and the search for ignitable liquid residues,
13 chromatographic techniques have been favoured by fire investigators for the
14 identification and confirmation of ignitable liquids and pyrolysis products [2]. Gas
15 Chromatographs coupled to different detectors such as FID [3] and the most versatile
16 MS [4] or MS-MS [5] have been widely used whereas liquid chromatographs fitted to
17 UV-VIS [6] detectors are less frequent. Spectroscopic techniques based on the use of
18 near or middle infrared spectra are scarce in the analysis of fire debris and they are
19 focused in the analysis of the pyrolysis products found in the decomposition of
20 materials such as plastics [7,8], wood [9] or paper [10]. This overwhelming use of
21 chromatographic techniques versus the spectroscopic ones is mainly due to the fact
22 that a more detailed description of the different components found in fire debris or
23 pyrolysis samples can be obtained with the former. This is unavoidable and necessary
24 when specific compounds need to be detected and/or quantified in the sample. This
25 information is of little or no use when identification of the materials involved in the

1 fire is needed. Identification of the different materials involved in a fire is of
2 paramount importance for reconstruction of fire or accident scenes. Fire or accident
3 investigators need to be able to obtain a clear picture of what was the situation and the
4 materials present prior to the event. In the case of aeroplane crashes the aircraft needs
5 to be literally reconstructed piece by piece. If the aircraft has been severely damaged
6 by fire, the identification and location of the different materials can be difficult and
7 takes time. In other forensic cases presence of foreign materials in a fire scene can be
8 of relevance to the case to indicate the intentionality of the event.

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

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

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

19 The aim of this research is the analysis of burnt plastic debris using Raman
20 spectroscopy assisted with multivariate analysis. The main plastics of interest are
21 polypropylene (PP), nylon (polyamide) and polystyrene (PS). These plastics occur in
22 many household items such as CD and DVD cases, carpets, textiles and furniture.
23 Thus suggesting that in the event of a domestic fire, these materials are highly likely
24 to be involved; therefore their analysis would be of much use to the both the fire scene
25 investigators and forensic scientists. When analysed, raw materials have a

1 characteristic spectrum or ‘band fingerprint’ which will change during the burning
2 process due to pyrolysis of the chemical compounds present in the material and also
3 maybe due to presence of accelerant residues in the fire debris. The use of ignitable
4 liquids may also change the spectra because of differences in calorific power of the
5 fuels, obtaining different pyrolysis products as a consequence of this. By studying the
6 change in the Raman spectra it may be possible to determine the nature of the sample
7 and identify different plastic materials in fire debris, even when different fuels have
8 been used. There is little information on the identification of plastic materials obtained
9 from fire scenes. To the best of our knowledge this is the first time Raman
10 spectroscopy is used in the analysis of fire debris for identification of plastic materials
11 burned with different ignitable liquids. The unique combination of Raman
12 spectroscopy together with the use of chemometrics allowed the identification of these
13 materials, even after having been burned. The study of the Raman behaviour of
14 different hydrocarbons and aromatic compounds obtained as pyrolysis products is also
15 scarce in the literature and focused in environmental applications [14].

16

17 **2. Materials and methods**

18 **2.1 Materials**

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

1 derivatives, namely butyl benzene and dimethyl benzene, and phenanthrene and
2 pyrene were also purchased from Sigma.

3 **2.2 Instruments**

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

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

17 **2.3 Methodology**

18 All of the samples were cut into six squares of approximately 5cm by 5cm in size. The
19 different materials were analysed using Raman microscopy in its original, unburned
20 state. Following this, the material was placed in an aluminium can, ignited and burned
21 in air with the different ignitable liquids of this study: petrol, diesel, kerosene and
22 ethanol; 5mL of the chosen ignitable liquid were added in each case, as a pool on non
23 porous materials and absorbed into the material in the case of porous ones. The length
24 of the burning process was timed and recorded and depended on the different
25 materials and fuels used. For the analysis, the materials were only burned for a

1 maximum of 5 minutes to standardise the burning process with the different ignitable
2 liquids (when considerable charring was observed and the ignitable liquid had
3 completely burned out) and extinguished by oxygen starvation. After burning, the
4 samples were left in the metal can to cool then placed in a labelled and sealed nylon
5 bag until analysis.

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

11

12 **3. Results and discussion**

13 **3.1 Analysis of raw and standard materials**

14 Plastics are combustible materials derived from petrol and they present similar
15 pyrolysis products when they burn. This implies that, once burned, some of these
16 plastics will present similarities in their Raman spectra with some common bands,
17 making their identification sometimes rather difficult. The three type of plastics
18 presented in this study, namely polystyrene (PS), polypropylene (PP) and nylon (Ny),
19 share some vibrational modes coming from the carbon framework in the range of
20 1443-1475 cm^{-1} , but differ in the presence of amide groups (for Ny) (1267 cm^{-1}) and
21 benzene groups (for PS) (998 cm^{-1}). These functional groups greatly help to identify
22 them and define their Raman spectra in the raw material.

23 Figure 1 shows the main Raman spectra obtained for all these materials prior to
24 burning them. This information will greatly assist in comparisons made with burnt
25 samples to identify which bands have been lost or gained. Figure 2 shows the Raman

1 shifts obtained for different middle-chain-size alkanes with chain length ranging from
2 C₁₁ to C₁₄. The main Raman bands observed for this group of compounds are: 1430
3 cm⁻¹, 1324 cm⁻¹, 1139 cm⁻¹, 1088 cm⁻¹ and 900 cm⁻¹ presenting in general an increase
4 of the peak intensity with increasing chain length for most peaks. This behaviour has
5 been previously reported in the literature in the case of alkanes [16] related to bands
6 close to 1440 cm⁻¹. Some of these vibrational modes can be found in PP when Figures
7 1c and 1d are analysed, but not in PS or Ny, supporting this idea of a vibrational mode
8 associated to carbon long chains. These bands will disappear after the burning process
9 helping us to interpret the type of alkane generated.

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

24 Finally The Raman shifts obtained from nylon were compared with those reported in
25 the literature for amide vibrations. Stuart [19] used the values to monitor how nylon

1 was affected by temperature. The conclusion of this study indicated that bands
2 corresponding to amide III would decrease the intensity with increasing temperature.
3 The nylon sample used in our study presents this band at 1267 cm^{-1} , allowing us to
4 identify the amide III group present in the polymer, but was not present in the burned
5 sample indicating that the amide group was either destroyed in the process or the
6 intensity considerably reduced to a point in which was undetectable.

7

8 **3.2. Analysis of burnt samples**

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

13 Figure 3.a and 3.b show typical Raman spectra obtained from a sample of a burnt CD
14 case made of polystyrene using petrol and diesel respectively. It can be observed in a
15 direct way the presence/absence of bands depending on the fuel used even when the
16 material burned is the same. Table I summarises all the peaks found for the different
17 fuels used and for all the materials in this research. The most common peaks found for
18 all the samples are those around $440\text{-}455\text{ cm}^{-1}$, $485\text{-}500\text{ cm}^{-1}$ and $550\text{-}565\text{ cm}^{-1}$. This
19 information will be of little value in order to cluster the different samples burned
20 under different conditions when performing the multivariate analysis using principal
21 component analysis (PCA), but it can offer a first clue about the nature of some of the
22 pyrolysis products obtained. Based on the data obtained from the literature [17], in the
23 region $400\text{ to }600\text{ cm}^{-1}$ we can identify medium intensity broad bands associated to
24 alkane vibrational modes. According to Stauffer [20], common pyrolysis products of
25 the combustion of PP are alkanes, alkenes and alkadienes following random scission.

1 These would be in line with the experimental evidence obtained for this plastic in our
2 study, but also suggests that alkanes will be a common and major pyrolysis product
3 for most of the plastics burned with the different fuels. These alkanes would be the
4 result of fragmentation in the polymer structure. However, based on the results
5 obtained from our analysis of linear chain alkanes in figure 2, we have to rule out their
6 presence as none of the characteristic bands obtained for the latter were found in the
7 fire debris analysed for all the polymers under study. This may indicate the presence
8 of branched carbon chains. This assumption can be supported by the fact that
9 branched carbon alkanes bands have been previously reported in the range 460-500
10 cm^{-1} (s-m) and 650-760 cm^{-1} (s), if attached to aromatic rings or alkene groups [16],
11 which is our case.

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

21 Other peaks can also be interpreted using the scarce Raman information given in the
22 literature for pyrolysis products. Thus, peaks found around 747 cm^{-1} in many of our
23 fire debris samples can be associated, according to Patnaik [16], to alkane vibrations.
24 Patnaik also identified peaks in the range 1029-1082 cm^{-1} as indicative of aromatic
25 compounds, especially substitution reactions occurring in poly benzene rings.

1 Wavenumbers around 1646 cm^{-1} were also associated to poly aromatic hydrocarbons
2 (PAH) according to our experimental work (see Figure 4). Some PAH, such as
3 phenanthrene pyrene or anthracene, presented bands around $1622\text{-}1648\text{ cm}^{-1}$. The
4 experiments performed on these PAHs can indicate that the region around 1600 cm^{-1}
5 and 1650 cm^{-1} correspond to polyaromatic vibrations of fused aromatic rings. The
6 band at 1646 cm^{-1} can be found in PS CD burned with all the ignitable liquids used in
7 this study (considering the shift due to the different chemical environment and
8 orientation). Fire debris obtained when PS foam was burned was scarce, as the
9 material was almost disintegrated during the burning process. Only in one case, when
10 burned with ethanol, a band at 995 cm^{-1} associated to a benzene ring could be
11 indentified. It is known that charred material due to its carbonaceous nature can help
12 to retain volatile organic compounds (VOC). If little material is left after combustion,
13 charred samples can hardly retain any of these compounds which could explain the
14 absence of bands and presence of bands associated to alkanes (maximum polymer
15 destruction \rightarrow shorter monomer chain size found).

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

1

2 **3.3 Chemometric analysis**

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

7 To answer this question the information obtained from the different burning
8 experiments (not averaged peaks) with the different plastic materials was used to
9 produce different score plots in PCA. The results of the multivariate analysis allowed
10 us to classify the different plastics for the different ignitable liquids used in the
11 experiments as can be seen in Figure 5. Figure 5a shows the clustering obtained with
12 the different plastic when burned with petrol. In this analysis, the PS CD case shows a
13 clear separation from the rest of the other plastics, which also clustered in different
14 groups. As shown on the figure, PC2 shows the most discriminatory power. The
15 percentage of variance obtained in this case was PC1=41% and PC2=26%. Figure 5b
16 shows the results obtained in the case of burning the samples with kerosene. In this
17 case PC2 is also the main discriminating axis, being PC1=43% and PC2= 17%. The
18 clusters can still be defined although there is some degree of overlapping between
19 them. This is also the case for the samples burned with ethanol (Figure 5c). There is a
20 clear cluster for PS CD case, with the rest of the clusters also showing some degree of
21 overlapping. The variance obtained was PC1=39% and PC2=24%. Finally, the results
22 obtained with diesel (Figure 4d) also showed a clustering pattern, with a cluster for
23 nylon clearly defined. In this case PC1 and PC2 have almost the same statistical
24 weight in the variance and the values obtained were PC1= 33% and PC2=32%. The
25 samples were also burned without any type of fuel to establish whether the presence

1 of the ignitable liquid could affect the obtained results (Figure 5e). It can be observed
2 that only in the case of nylon and polystyrene from the CD case there is some degree
3 of differentiation between the fire debris obtained with the different samples. In the
4 rest of the cases there is a high degree of overlapping between the different samples
5 (indicated by the numeral). It can also be seen that in these cases the identification of
6 samples would be very difficult. The results for the variation in the PCA was PC1=
7 38% and PC2=20%. Other combinations using the different PCs obtained in the
8 analyses were tried and PCAs based on PC1 and PC2 resulted to produce the best
9 discriminative plots.

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

22 The results obtained in this research can open an opportunity to further investigate the
23 use of Raman spectroscopy in fire investigations. There are still many questions that
24 remain unanswered and further research is needed. Some areas for future
25 improvements imply the use of silver or gold colloids to quench the fluorescence in

1 order to obtain much more information on the different compounds present in the
2 debris by using SERS. Sensitivity can also be improved and more bands from
3 pyrolysis products might be detected, thus improving the chances for a much better
4 and finer clustering using PCA analysis. Another factor to explain the differences
5 observed in the clustering patterns of polymers is related to the use of fire retardants.
6 By law, polymers used in everyday and industrial products need to incorporate them
7 in their composition to improve their resistance to fire. This will certainly have an
8 impact in the way they burn and in the pyrolysis products obtained. This is not
9 necessarily a problem as they will also incorporate differences that may help to
10 discriminate between polymeric materials with the same chemical composition. These
11 fire retardants can explain the differences observed in our study, but more research in
12 this area is also needed. In our study it was decided to use real samples rather than
13 standards of polymeric substances trying to obtain a more realistic picture and present
14 a real possibility of using Raman to fire investigators and forensic scientists.

15 **4. Conclusions**

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

1

2 **5. Acknowledgements**

3 The authors want to thank The Nuffield Foundation UK for economic support in the
4 form of a Nuffield Foundation Science Bursary to one of the authors, which allow her
5 to develop part of the work shown in this paper.

6

7 **6. Literature**

8 [1] A.D. Pert, M.G. Baron, and J.W. Birkett, The analysis of smoke and accelerants
9 from fire scenes, *J. Forensic Sci.* 51 (2006) 1033-1049.

10 [2] K. L. Sobeih, M.G. Baron, and J. Gonzalez-Rodriguez, Recent trends and
11 developments in pyrolysis-gas chromatography, *J. of Chrom. A* 1186 (2008) 51-66.

12 [3] M.J. Camp, Analytical Techniques in Arson Investigation, *Anal. Chem.* 52 (1980)
13 422-426.

14 [4] W. Bertsch, Analysis of Accelerants in Fire Debris -data Interpretation, *Forensic*
15 *Sci Rev.* 9 (1997) 1-22.

16 [5] B. deVos B, M. Froneman, E. Rohwer, and D. Sutherland, Detection of petrol
17 (gasoline) in fire debris by gas chromatography/mass spectrometry/mass spectrometry
18 (GC/MS/MS), *J Forensic Sci.* 47 (2002) 736-756.

19 [6] V.R. Dhole, and G.K. Ghosal, Detection and characterisation of petroleum based
20 accelerants in fire debris by HPLC, *J. Liquid Chrom.* 18 (1995) 1767-1786.

21 [7] J.M. Kanabus-Kaminska, G.D. Loughheed, D. W. Carpenter, and D.A. Torvi,
22 Determination of major and minor components of smoke from full-scale fire tests of
23 furnishings by FTIR spectroscopy, *Fire and Materials Conference* (2001) 407-17.

24 [8] L.C. Speitel, Fourier Transform Infrared Analysis of Combustion Gases, *J. Fire*
25 *Sci.* 20 (2002) 349-371.

- 1 [9] S. Wang, K. Wang, Q. Liu, Y. Gu, Z. Luo, K. Cen, and T. Fransson,
2 Biotechnology Advances, Comparison of the pyrolysis behavior of lignins from
3 different tree species 27 (2009) 562-567.
- 4 [10] A. Mendez, J.M. Fidalgo, F. Guerrero, G. Gasco, Characterization and pyrolysis
5 behaviour of different paper mill waste materials J. Anal.Appl. Pyrol. 86 (2009) 66-
6 73.
- 7 [11] T. Furukawa, H. Sato, Y. Kita, K. Matsukawa, H. Yamaguchi, S. Ochiai, and Y.
8 Ozaki, Raman mapping study of Polyethylene/Polypropylene blends, Polymer Journal
9 38 (2006) 1127-1136.
- 10 [12] D.S. Zhou, N. Xu, L. Li, G. Ji, and G. Xue, Surface Reactions on Polymer Thin
11 Films Studied by Surface-Enhanced Raman Scattering, J.Phys.Chem. B 107 (2003)
12 2748-2751.
- 13 [13] Y. Li, Y. Fan, and J. Ma, Thermal, physical and chemical stability of porous
14 polystyrene-type beads with different degrees of crosslinking, Polymer Degradation
15 and Stability 73 (2001) 163-167.
- 16 [14] C.L. Jones, K.C. Bantz, C.L. Haynes, Partition layer-modified substrates for
17 reversible surface-enhanced Raman scattering detection of polycyclic aromatic
18 hydrocarbons, Anal Bional Chem 394 (2009) 303-311.
- 19 [15] R. Rakotomalala, "TANAGRA: a free software for research and academic
20 purposes", in Proceedings of EGC'2005, RNTI-E-3, vol. 2, pp.697-702, 2005. (in
21 French).
- 22 [16] P. Patnaik, Dean's Analytical Chemistry Handbook, 2nd Edition, Mc Graw-Hill
23 Ed, New York, 2004.
- 24 [17] Horiba Jobin Yvon, Technical note: Raman Spectroscopy for Analysis and
25 Monitoring, <http://www.jobinyvon.com/usadivisions/Raman/applications/bands.pdf>

1 [last accessed: 23/12/09].

2 [18] .T. Carron, and B.J. Kennedy, Molecular-specific chromatographic detector using
3 modified SERS substrates, *Anal. Chem.* 67 (1995) 3353-3356.

4 [19] B.H. Stuart, A Fourier transform Raman study of water absorption by Nylon 6,
5 *Polymer bulletin* 33 (1994) 681-686.

6 [20] E. Stauffer, Sources of interference in fire debris analysis in *Fire Investigation*,
7 N. Daeid Ed., CRC Press, 2004, p.191.

8 **7. Captions**

9 **7.1 Table captions**

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

13

14 **7.2 Figure captions**

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

17

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

20

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

23

24 Figure 4. Raman spectra of (a) phenanthrene, (b) pyrene and (c) anthracene

25

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

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

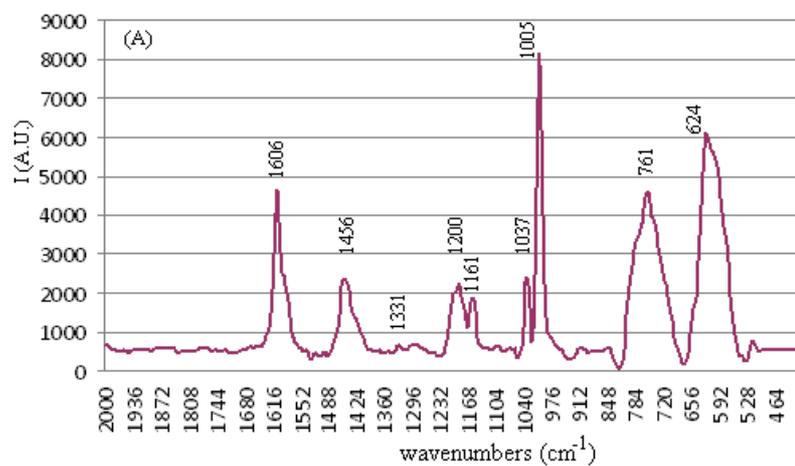
24

25

1 Figure 1a

2

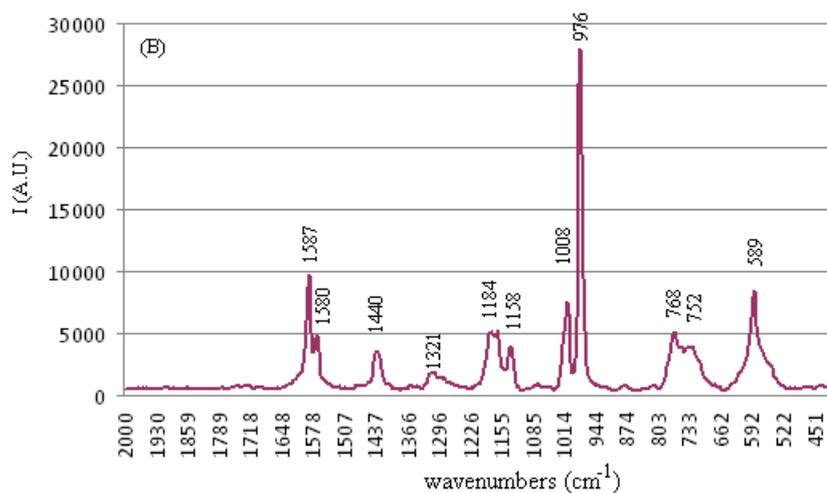
3



4

5 Figure 1b

6



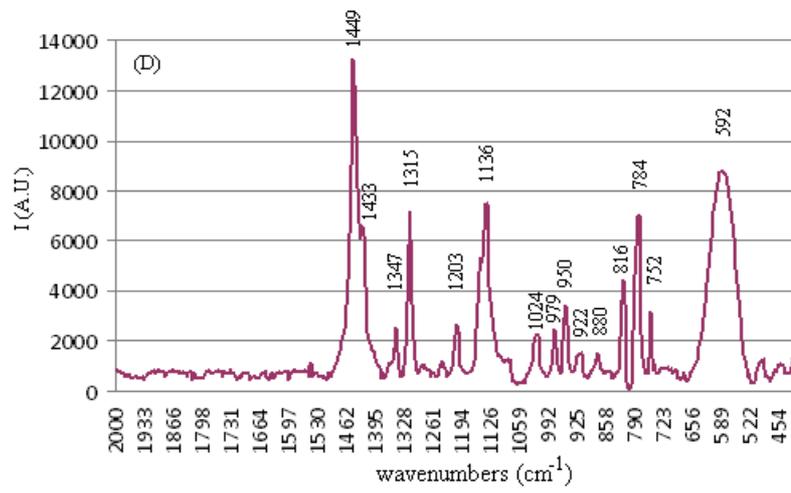
7

8

9

1 Figure 1c

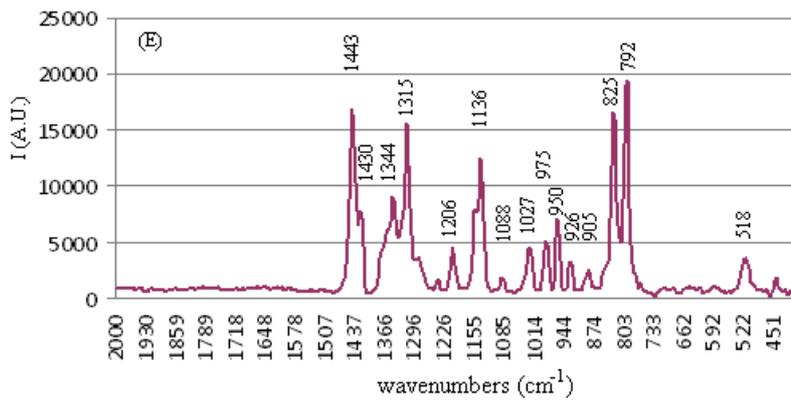
2



3

4

5 Figure 1d



6

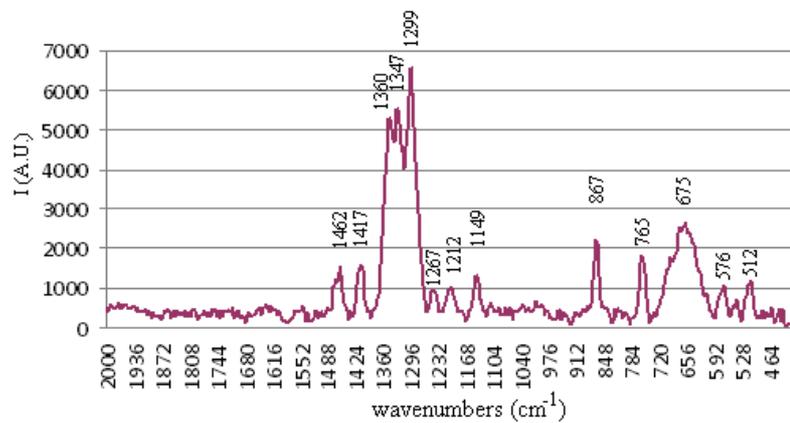
7

8

9

1 Figure 1e

2



3

4

5

6

7

8

9

10

11

12

13

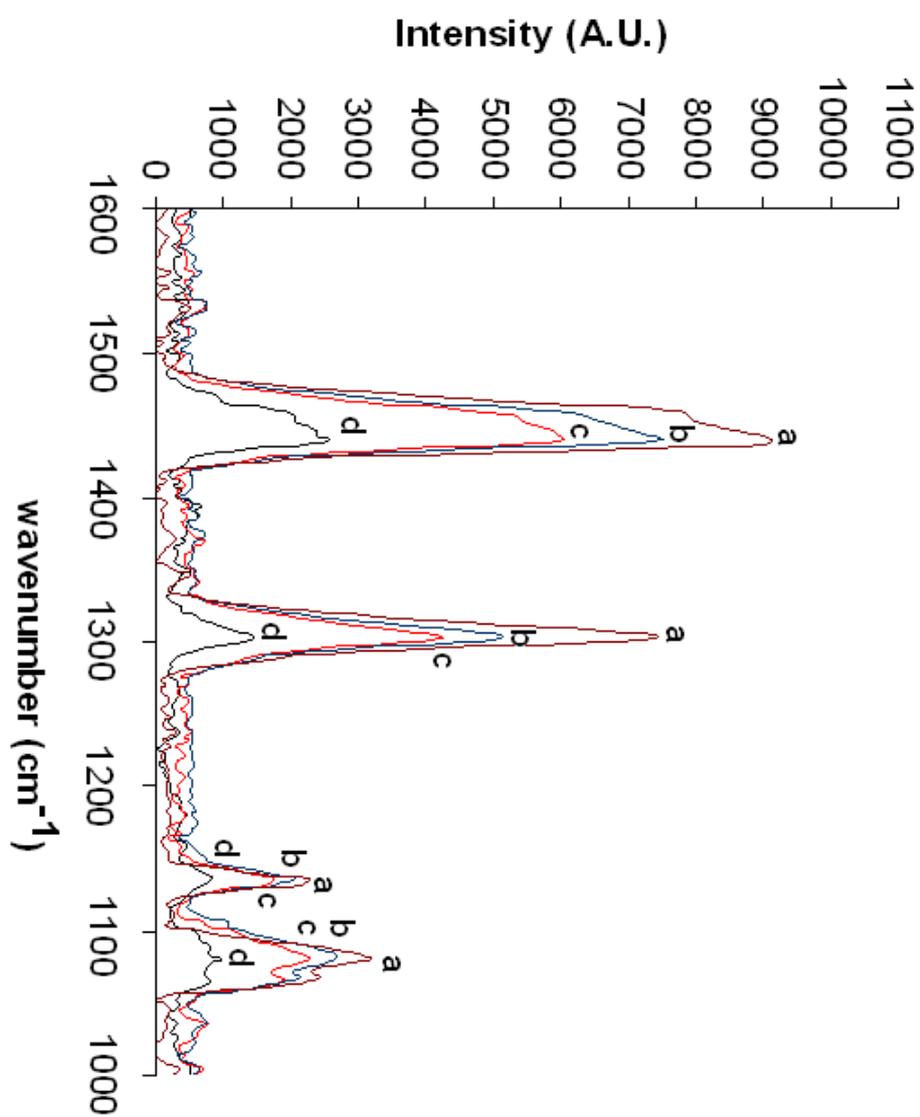
14

15

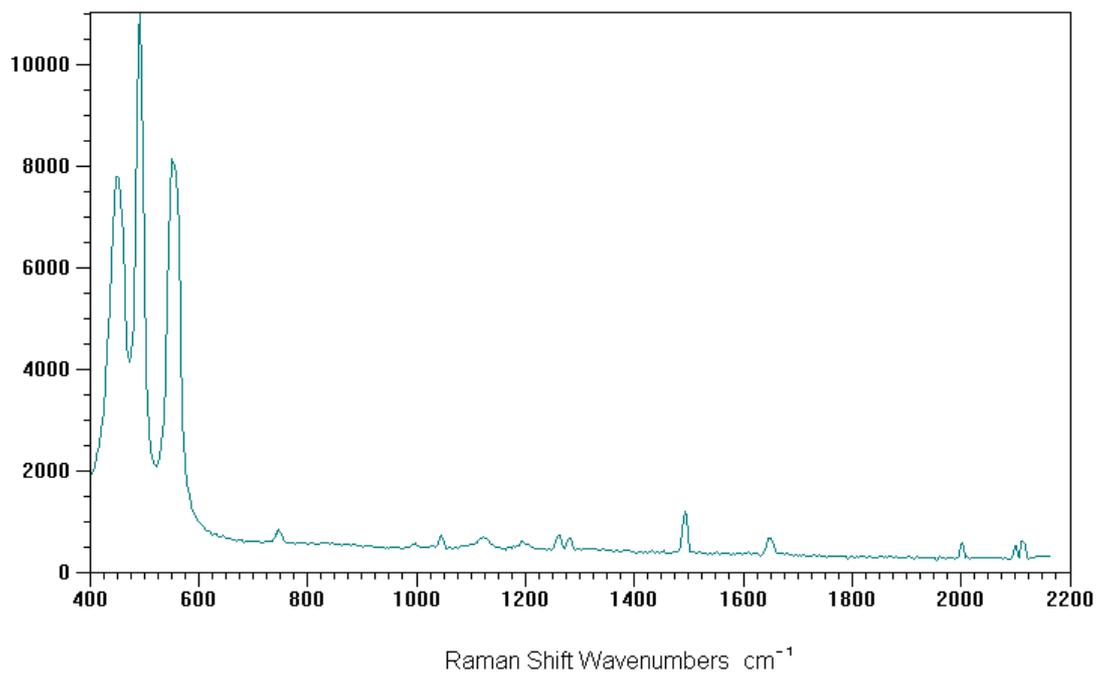
16

17

1 Figure 2



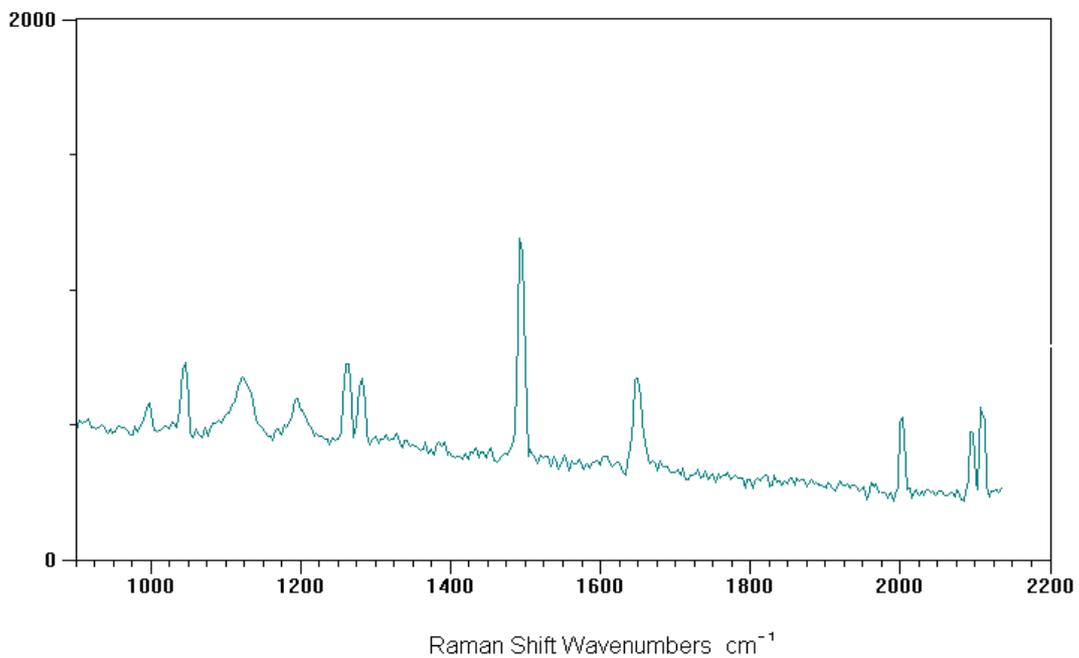
1 Figure 3a



2

3

4 3a zoom



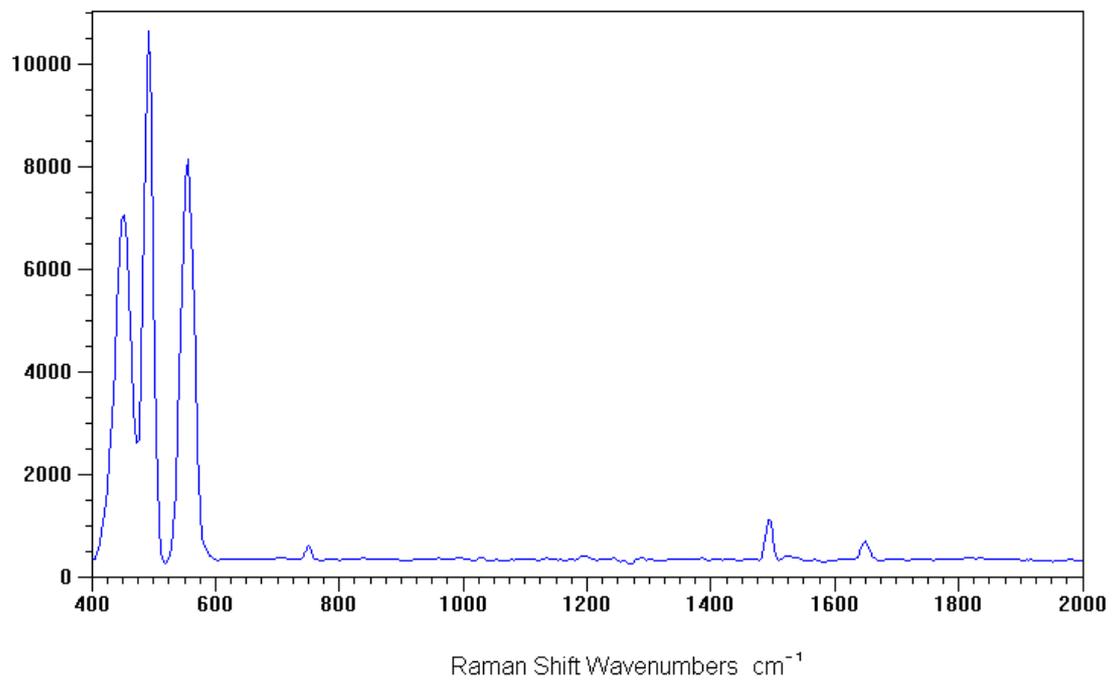
5

6

7

1 Figure 3b

2



3

4

5

6

7

8

9

10

11

12

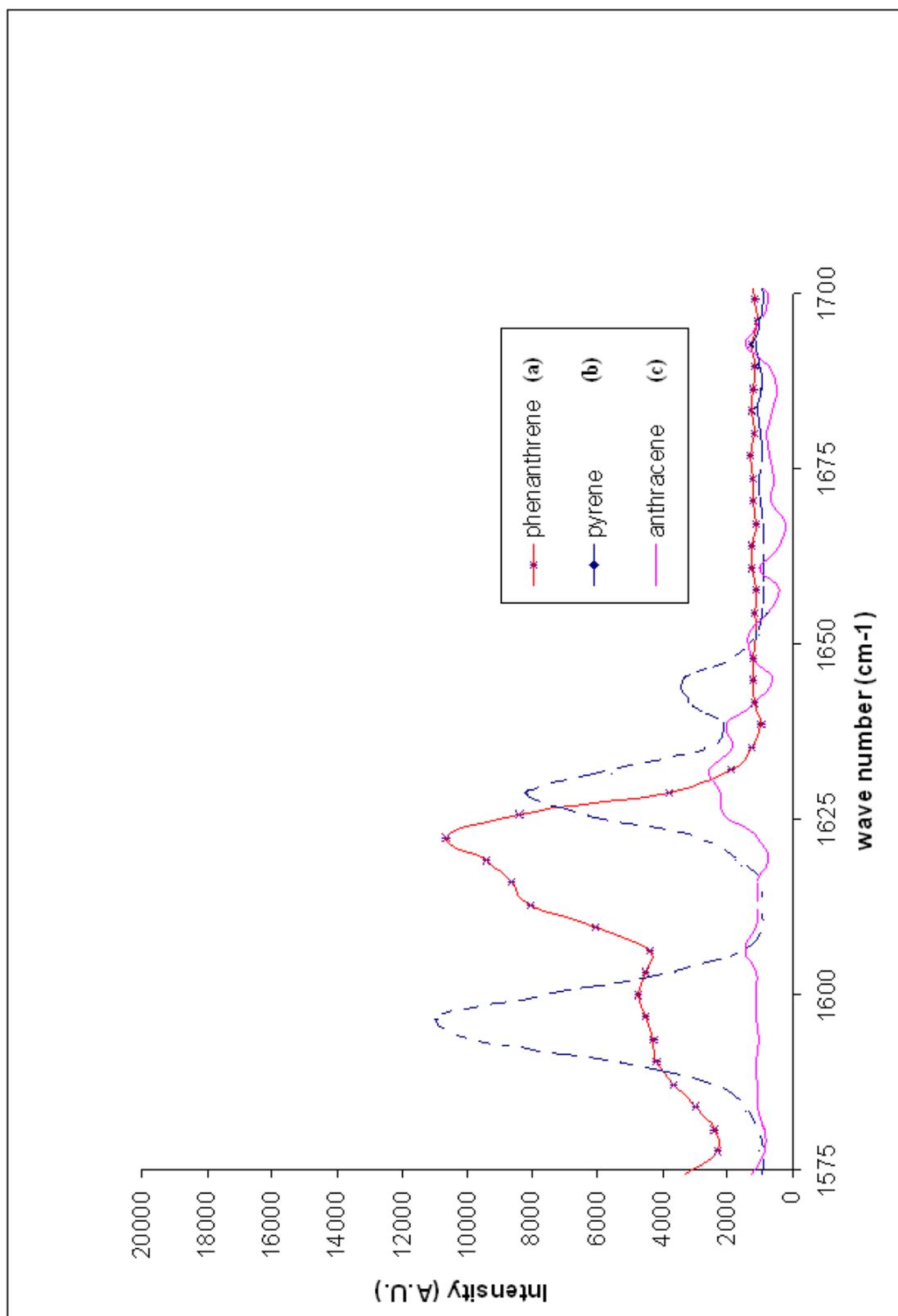
13

14

15

16

1 Figure 4

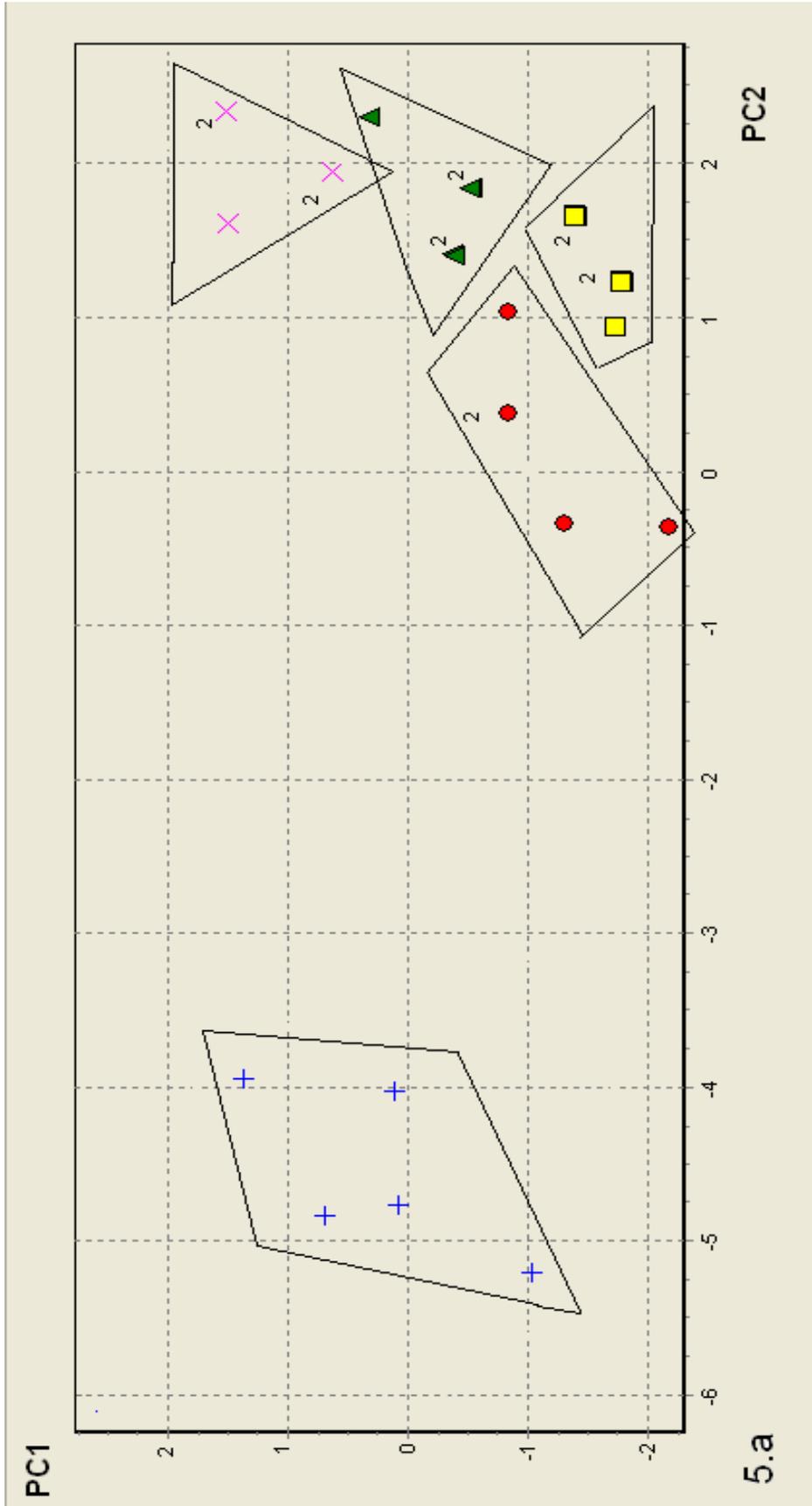


2

3

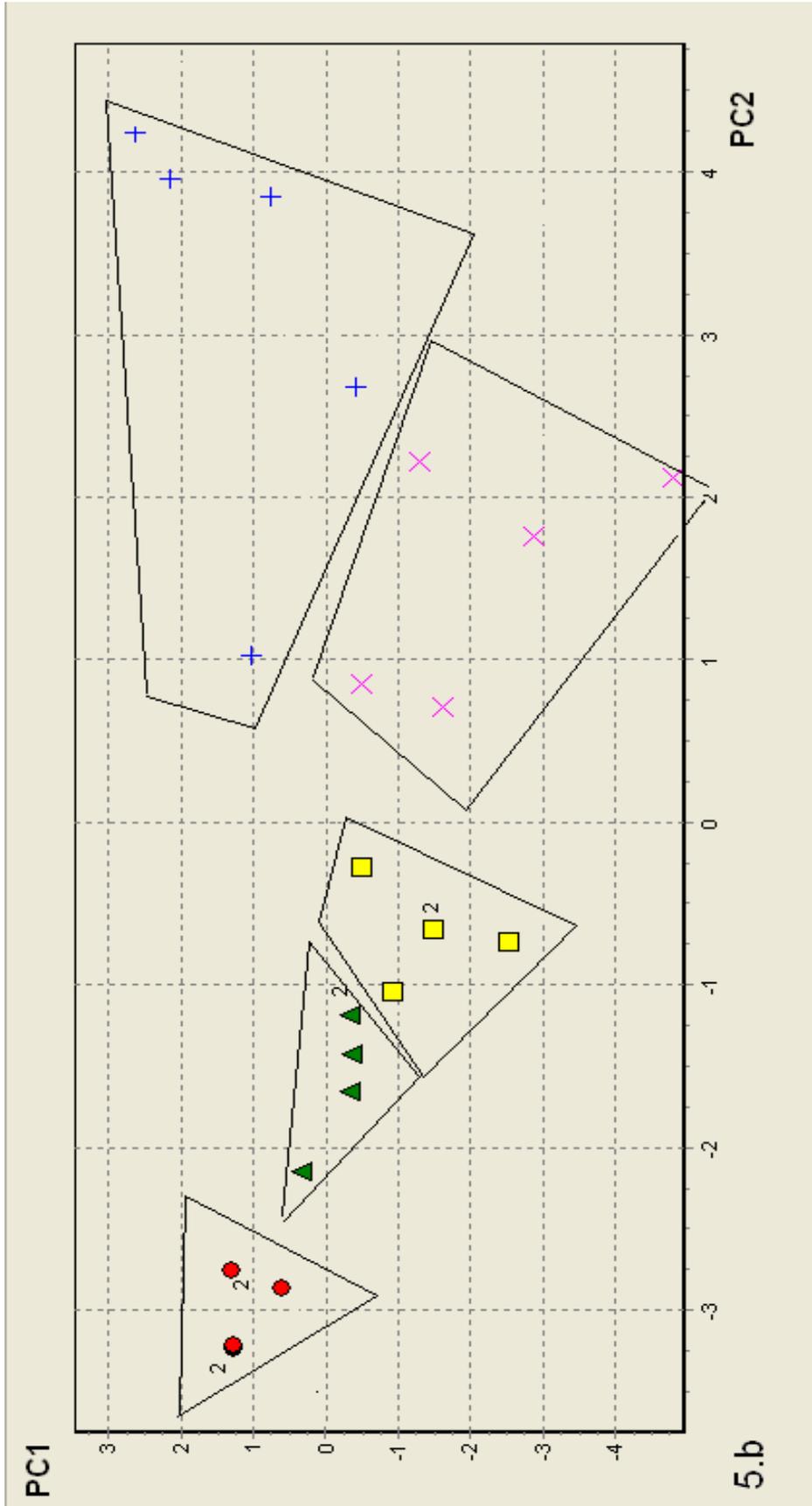
4

1 Figure 5a



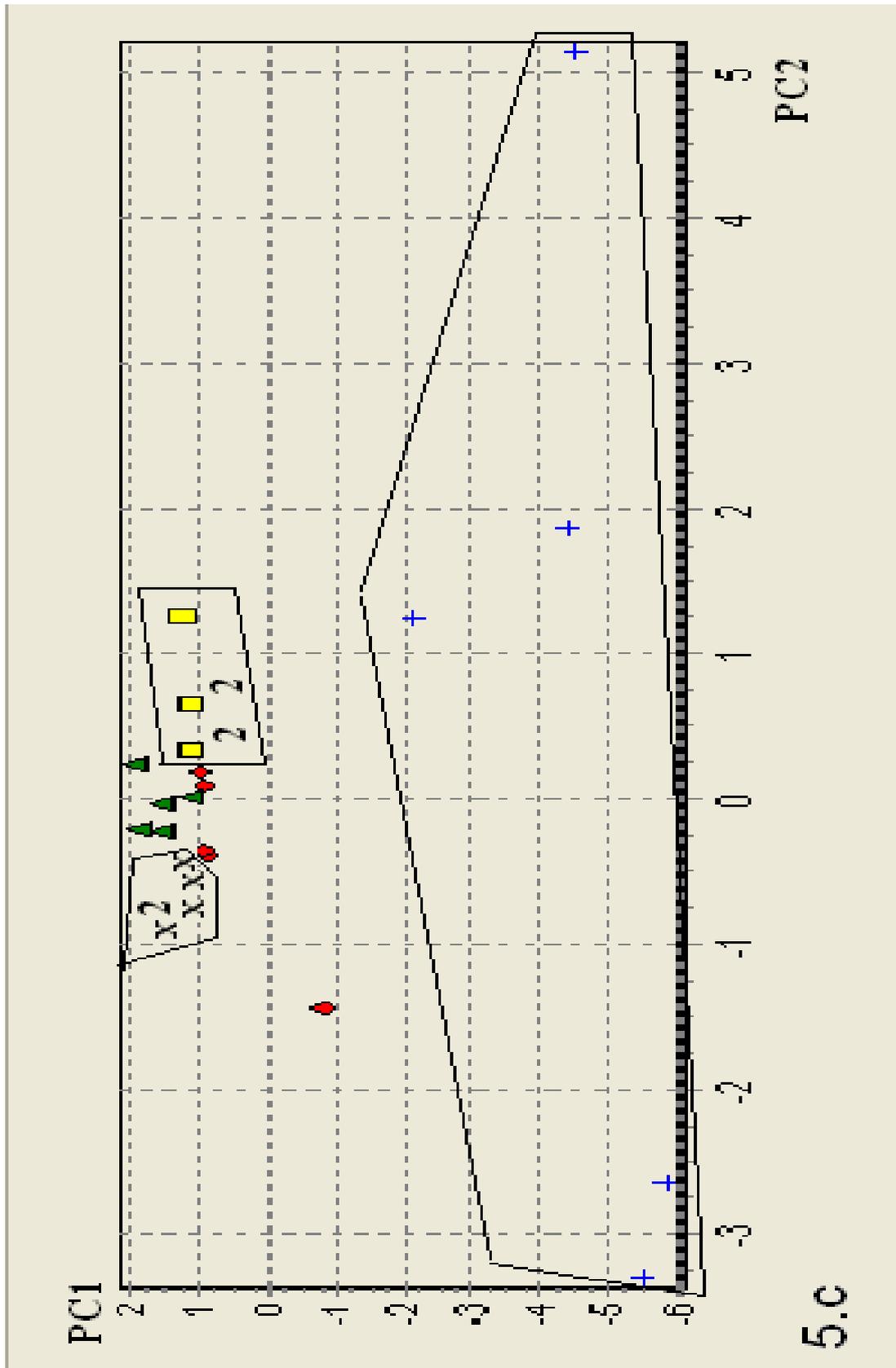
2

1 Figure 5b



2

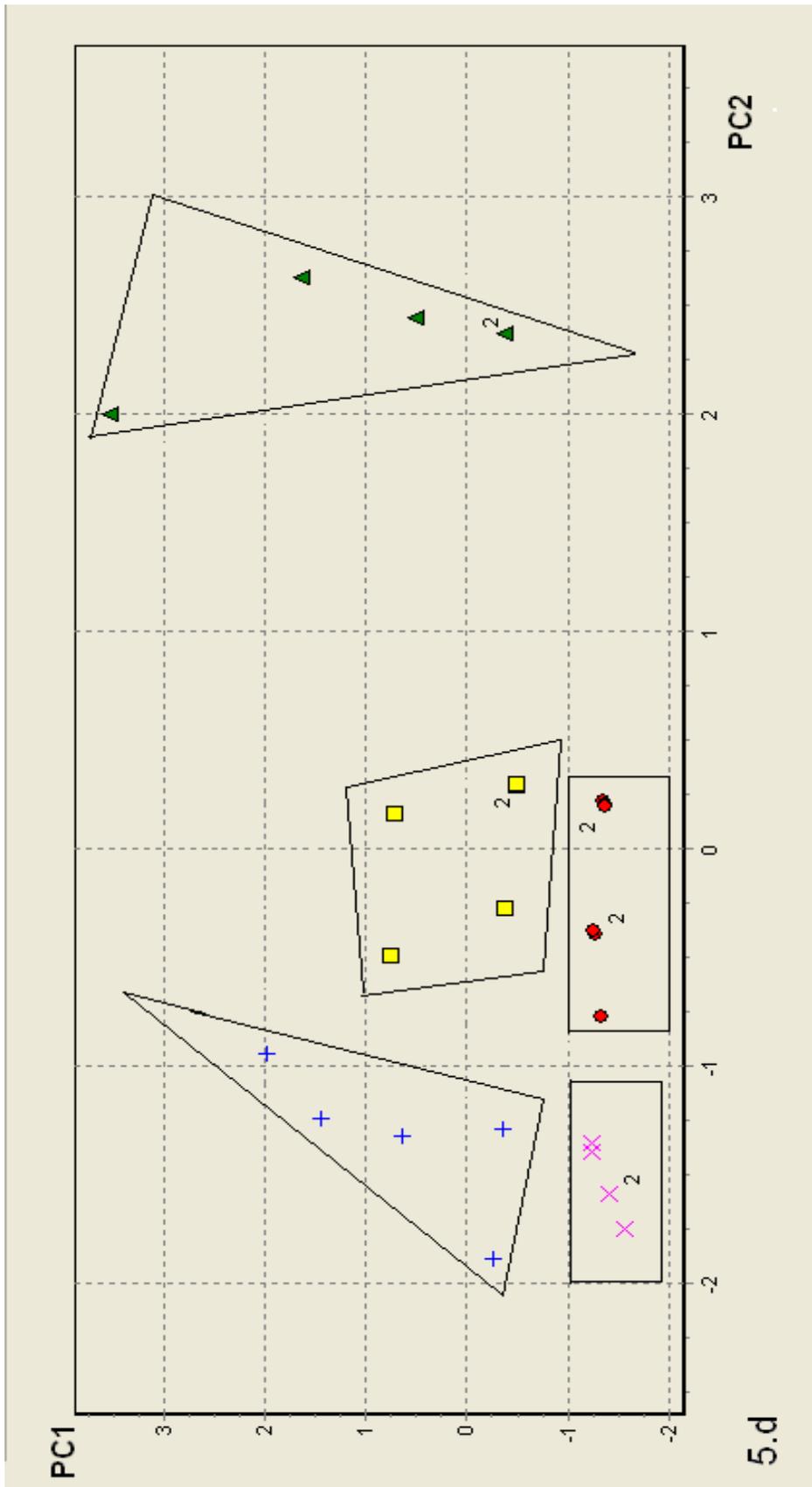
1 Figure 5c



2

3

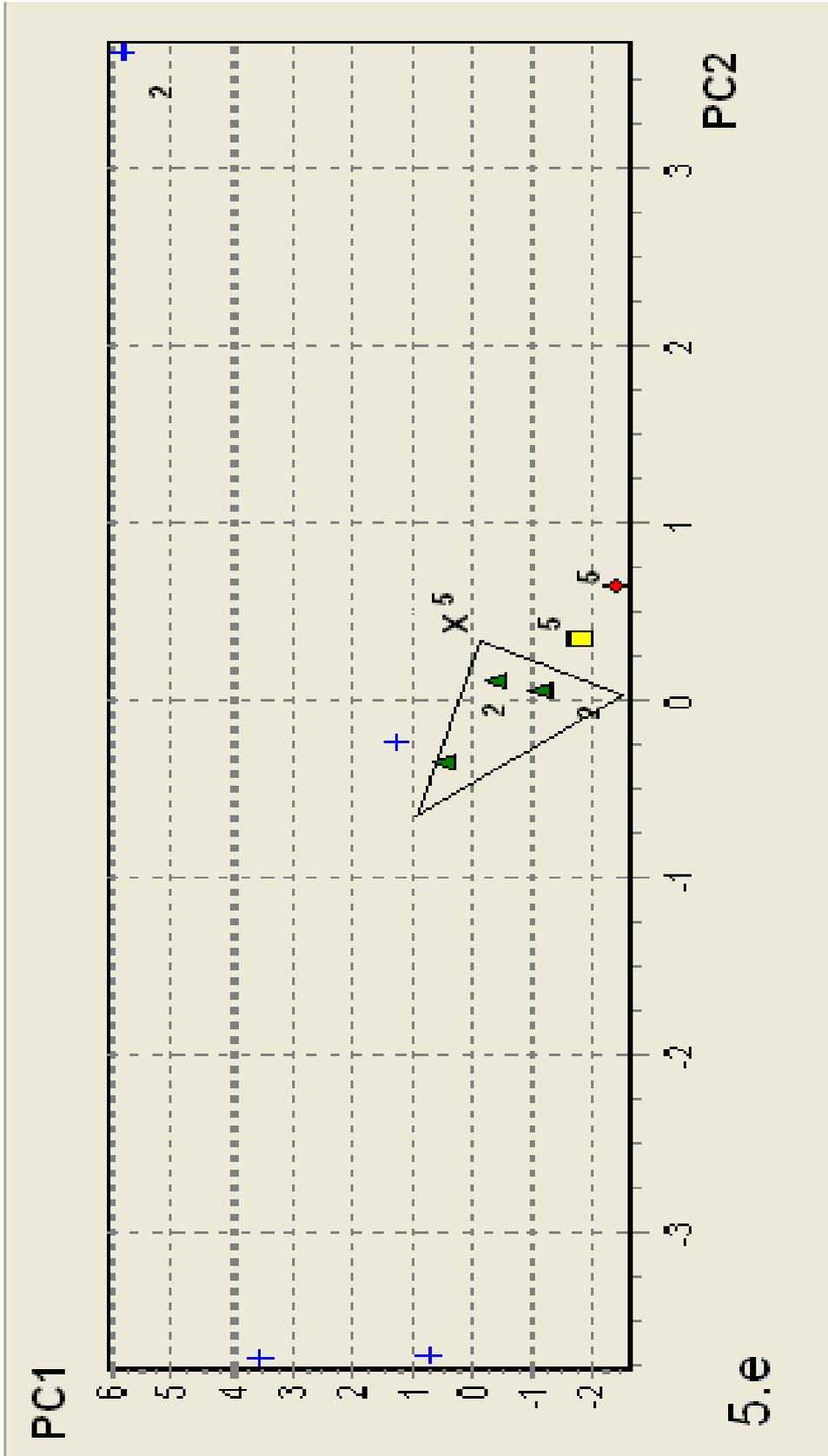
1 Figure 5d



2

3

1 Figure 5e



2

3

- 1 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
 2 minimum of 3 and a maximum of 8)

Sample/ cm ⁻¹	440- 455	485- 500	550- 565	740- 755	950- 1005	1040- 1050	1185- 1205	1255- 1270	1280- 1300	1490- 1500	1645- 1655	2005- 2025	2095- 2109	2110- 2115	2120- 2130
Petrol															
PS foam	448	490	551							1493					
PS CD	448	490	551	752	993	1044	1191	1264	1283	1495	1652	2014	2100	2110	2121
PP carpet	448	490	554	744						1495		2018			
PP DVD			554	747											
Nylon	442	490	554												
kerosene															
PS foam	448	491	552							1492					2127
PS CD	446	490	551			1047		1263	1284	1496	1653	2011	2099	2113	
PP carpet			551	747											
PP DVD	448	490	552			1043		1260		1494		2019			2122
Nylon	446	490	554							1490					

Ethanol															
PS foam	448	490	554		995										
PS CD	448	490	554	749	992		1196	1266		1493	1655	2018			
PP carpet	453	491	554							1493					
PP DVD	448	490	554	747											
Nylon	450	490	557												
Diesel															
PS foam	446	491	552							1490					
PS CD	448	490	551	748						1495	1649				
PP carpet	448	492	551												
PP DVD	448	490	554	747											
Nylon	448	490	554	747						1495					

1
2
3