

## Forensic isotope ratio mass spectrometry of packaging tapes

James F. Carter,\* Polly L. Grundy, Jenny C. Hill, Neil C. Ronan, Emma L. Titterton and Richard Sleeman

Mass Spec Analytical Ltd., Building 20F, Golf Course Lane, PO Box 77, Filton, Bristol, UK BS99 7AR. E-mail: jimc@msaltd.co.uk

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Pressure sensitive adhesive tape (brown parcel tape) is employed in a great many criminal activities such as the restraint of individuals during robbery and offences against the person, the enclosure of explosive devices and the packaging and concealment of controlled drugs. Packaging materials are ubiquitous in modern society and are produced in such vast quantities that it is increasingly difficult to distinguish between different products or to link materials to a common source. This study demonstrates the potential of stable isotope ratio mass spectrometry to characterise parcel tapes based on a number of properties. The carbon isotopic signature, derived from the substrate polymer, associated additives and adhesive is highly characteristic of a particular tape and allows samples from different sources to be readily distinguished. Further discrimination may be achieved by the incorporation of deuterium and oxygen isotopic data and by analysis of the isolated backing polymer. Recovery of intact tape from simulated forensic samples proved straightforward and the isotopic signature of the tape did not appear to be affected by adverse storage conditions.

### Introduction

Recent years have seen an increase in the forensic use of stable isotope ratio techniques,<sup>1</sup> especially for the characterisation of natural, and modified natural, controlled substances, *e.g.*, heroin<sup>2</sup> and cocaine,<sup>3</sup> in which the stable isotopic signature is largely controlled by growth conditions such as nutrient and moisture availability.<sup>4</sup> The techniques have also been applied to synthetic controlled substances such as amphetamines,<sup>5</sup> in which the isotopic signature is dependent upon the synthetic conditions employed.<sup>6</sup> Although recently adopted, these techniques are becoming acceptable to the wider forensic community and provide a means of linking controlled substances to a common source or supply when other techniques, *e.g.*, impurity profiling, are less applicable. Of equal interest to law enforcement authorities are the packaging materials in which controlled substances are inevitably seized.<sup>7</sup> Because packaging materials are ubiquitous and frequently lack any distinct markings, it is often difficult to provide an unequivocal link between items seized at different times and locations.

Whilst small scale drug trafficking can be considered a "high volume" crime, packaging materials are also associated with "high value" crimes, such as murder, assault and terrorism. In such cases, packaging materials can play a wide range of roles, for example, to bind an individual during a robbery, assault or murder or to contain an explosive device. It has been reported<sup>7</sup> that the packaging material most commonly associated with crime is pressure sensitive adhesive (PSA) tape, often referred to as "brown parcel tape". This tape typically comprises a polypropylene or poly(vinyl chloride) (PVC) film, an intermediate layer and an acrylic or natural rubber adhesive. Spectroscopic techniques, such as UV/Vis<sup>8</sup> and FTIR<sup>8,9</sup> may be applied to determine the nature of both the backing polymer and the adhesive. Such analyses are often used in combination with techniques such as XRF<sup>10</sup> or ICP-MS<sup>11</sup> to determine the presence of certain trace metals as a means of discriminating between different brands of tape. Due to the low abundance of metals within PSA tape, the latter techniques require relatively large samples (*ca.* 10 cm<sup>2</sup> in area) and special handling conditions to avoid contamination.<sup>10</sup> Conventional

optical techniques may be used to compare PSA tapes,<sup>8</sup> but are of little probative value since polymer films are produced in such quantity and with such uniformity that few obvious differences exist. These techniques are, however, of value when comparing pieces of tape separated by cuts or tears.<sup>12</sup> Although pyrolysis-GCMS (Py-GCMS) is frequently employed to distinguish subtle differences between polymer compositions and has been applied to PSA tape,<sup>9</sup> the chromatograms are typically extremely complex and require elaborate statistical analysis to distinguish differences.<sup>13</sup>

### Experimental

Five rolls of commonly available brands of PSA tape were purchased from local suppliers and designated P1–5. A further five samples of PSA tape were obtained from parcels delivered to the laboratory prior to experimental work. These were carefully removed from the parcels to ensure that no paper, or other materials, adhered to the adhesive and were designated P6–10.

Samples were taken from an inner layer of the roll or parcel, where the adhesive was in contact with an underlying layer of tape. Before further preparation the tape was inspected to assure that the adhesive was intact and that no extraneous material had adhered to it. These samples were designated as "untreated". A portion of tape from each batch was treated by immersion in several hundred ml of solvent (acetone (Fisons Distol, Loughborough, UK) and petroleum spirit (40–60 °C, BDH General Purpose Reagent, Poole, UK)) in an ultrasonic bath for 15 min each, followed by drying in air at ambient temperature. This process removed the adhesive and binder, leaving the polymeric backing material. These samples were designated as "treated". Small samples of "untreated" and "treated" PSA tapes were analysed for  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotopic content. Approximately 1 mm<sup>2</sup> samples of tape were analysed, equivalent to between 100–200  $\mu\text{g}$  of material. Samples were prepared on an aluminium surface, which was cleaned with acetone between samples and cut with Throwaway knives (Stanley, Sheffield, UK).

In order to assess the affects of use and storage on the

isotopic composition of PSA tape, parcels were prepared using tapes P1, 2, 3 and 5. Parcels comprised a plastic supermarket carrier bag, stuffed with shredded paper and bound thoroughly with at least three layers of PSA tape. To prevent easy detection by sniffer dogs, packages containing illicit drugs, banknotes or explosives are typically well wrapped with several layers of tape. Two parcels were prepared from each of the four brands of tape and stored either in a closed drawer or submerged in water for several weeks. The latter condition was intended to simulate the common practice of concealing packages of drugs in water tanks or cisterns. Samples of PSA tape were taken from the central layer of parcel wrappings and visually examined for damage or contamination prior to cutting and analysis. Providing that the tape was wound at least twice around the parcel, such that the second layer partially covered the first, there was sufficient unexposed tape available for analysis.

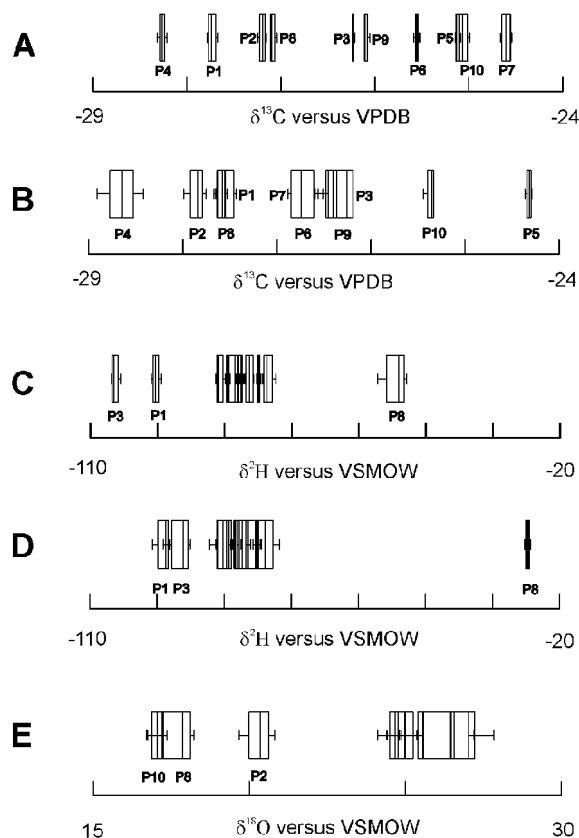
All isotopic measurements were performed using a ThermoFinnigan DeltaXP isotope ratio mass spectrometer (IRMS) via a ConFlo III interface. Carbon isotopic measurements were performed using a ThermoElectron Flash 1112 elemental analyser. Samples were crimped into tin capsules (Elemental Microanalysis, Okehampton, UK) and introduced using an AS200 autosampler. The oxidation reactor, comprising chromic oxide and silver/cobaltous oxide, was maintained at a temperature of 900 °C and the reduction reactor, comprising electrolytic copper, was maintained at 680 °C. Helium carrier gas was maintained at a flow of 150 ml min<sup>-1</sup> and a 5 second pulse of oxygen (BOC Research Grade N5.5) was introduced at a flow rate of 175 ml min<sup>-1</sup>. Water was removed from the evolved gases by anhydrous magnesium perchlorate (Elemental Microanalysis). The carbon isotopic content of each sample was determined four times. The isotopic composition was referenced against gaseous carbon dioxide (BOC CP Grade N4.5) which was, in turn, calibrated against PEF1 polyethylene foil (National Institute for Standards and Technology (NIST) Reference Material (RM8540)).

Hydrogen and oxygen isotopic measurements were performed using a ThermoFinnigan TC/EA high temperature elemental analyser. Samples were crimped into silver capsules (Elemental Microanalysis) and introduced using an AS200 autosampler. The pyrolysis reactor, comprising an alumina tube lined with glassy carbon, was maintained at a temperature of 1350 °C with a helium carrier gas flow of 90 ml min<sup>-1</sup>. Hydrogen and carbon monoxide, pyrolytically formed in the reactor, were separated using a gas chromatography column containing 5 Å molecular sieve maintained at a temperature of 90 °C. Each sample was analysed a total of five times but the first result was discounted to allow for memory effects associated with the glassy carbon. Isotopic compositions were referenced against gaseous hydrogen (BOC Research Grade N5.5) and carbon monoxide (BOC Research Grade N3.7), which were in turn calibrated against PEF1 polyethylene foil (NIST RM8540) and NBS19 calcium carbonate (NIST RM8544).

Data were acquired and processed using ISODAT NT 2.0 software. Isotopic values are reported relative to the international standards<sup>14</sup> Vienna PeeDee Belemnite (VPDB) for carbon and to Vienna Standard Mean Ocean Water (VSMOW) for deuterium and oxygen. All statistical manipulations of the acquired data were performed using SYSTAT 7.0 for Windows.

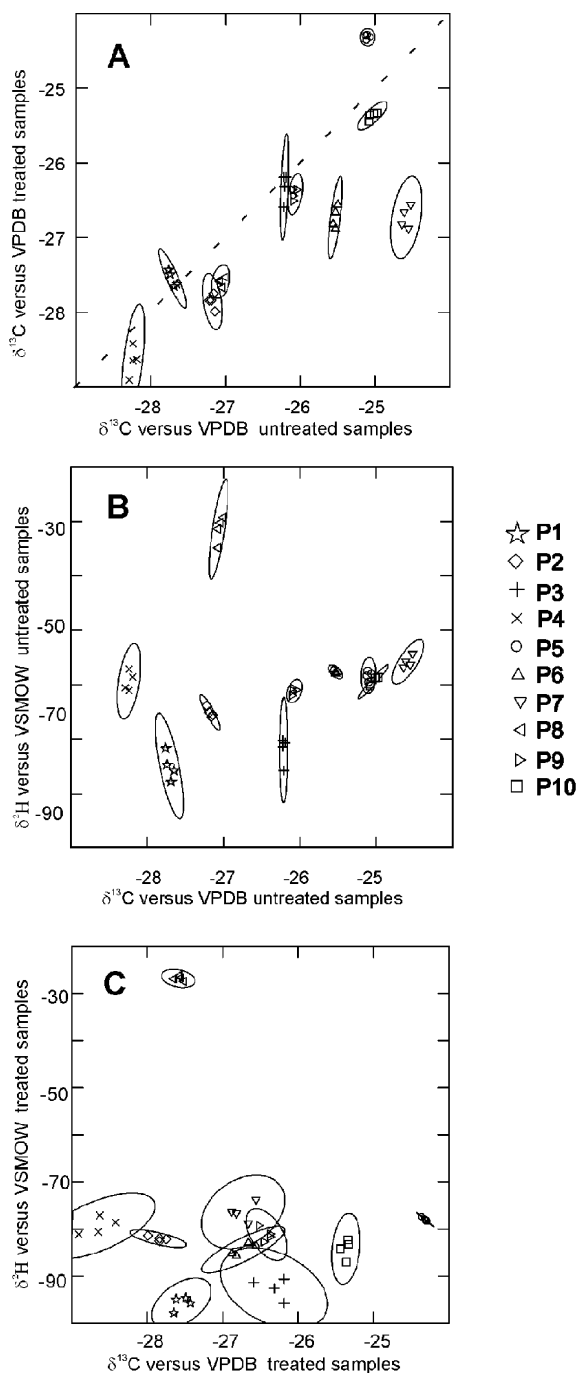
## Results and discussion

The  $\delta^{13}\text{C}$  data for the untreated PSA tapes are represented as a box plot in Fig. 1A. Samples are referred to as P1 to P10 and are the same in all figures. The length of each box shows the



**Fig. 1** Box plots representing  $\delta^{13}\text{C}$  data for untreated samples (A) and treated samples (B),  $\delta^2\text{H}$  data for untreated (C) and treated samples (D) and  $\delta^{18}\text{O}$  data for untreated samples (E).

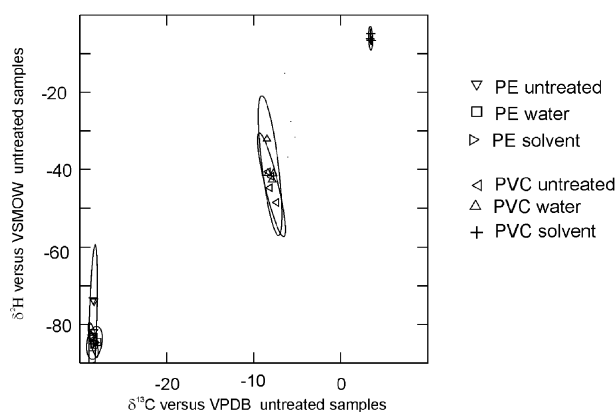
range within which the central 50% of the values fall and the “whiskers” the minimum and maximum values. Using this comparison the untreated samples form nine discrete groupings, only P5/P10 being indistinguishable. The standard deviation of the analytical results was typically 0.03%, which implies that the tape samples were homogeneous and that representative samples were taken without external contamination. In contrast, the box plot corresponding to the treated PSA tapes (Fig. 1B) shows only six discrete groupings with greater uncertainties, typical standard deviation being 0.16%. One grouping comprised four samples, which may indicate a common source for the backing material used to manufacture the tapes. Samples P5/P10 are indistinguishable when considering the untreated  $\delta^{13}\text{C}$  values but are readily distinguished once the adhesive is removed. Interpretation of these data is assisted by Fig. 2A, which shows a plot of the  $\delta^{13}\text{C}$  data for the treated *versus* the untreated tape (with 95% confidence ellipses). This plot emphasises the greater spread of data recorded for the treated tape (Y-axis) and also the change in isotopic value when the adhesive is removed. The diagonal broken line indicates a 1 : 1  $\delta^{13}\text{C}$  ratio for the untreated and treated samples, with the majority of samples falling below this line. This indicates that the samples become isotopically lighter when the adhesive is removed and that the adhesive is therefore enriched in  $^{13}\text{C}$  with respect to the backing material. This form of data presentation also provides a useful means to characterise the samples, since coincident ellipses represent tapes for which both the backing material and the adhesive are indistinguishable with respect to  $\delta^{13}\text{C}$  content. Samples P3/P9 are ambiguous when using this comparison but are distinguished when considering only the box plot (Fig. 1A). This results from the uncertainty associated with the  $\delta^{13}\text{C}$  measurements of the treated tape, which causes broadening of both the box plot (Fig. 1B) and the combined data confidence ellipses (Fig. 2A). Assuming that all



**Fig. 2**  $\delta^{13}\text{C}$  data for untreated samples versus treated samples (A),  $\delta^2\text{H}$  data versus  $\delta^{13}\text{C}$  data for untreated samples (B) and  $\delta^2\text{H}$  data versus  $\delta^{13}\text{C}$  data for treated samples (C).

instrumental parameters are constant, there are a number of explanations for this effect, including incomplete removal of the adhesive or residual solvent absorbed by the polymer matrix during removal of the adhesive. Neither of these scenarios appears likely since visual examination of the treated tape revealed no discernable deposits and the  $\delta^{13}\text{C}$  value of the backing material was found not to change during storage at elevated temperature. A more likely explanation is that the solvent extraction procedure removed additives, such as plasticiser, or low molecular weight oligomer from the polymer matrix, in addition to the surface adhesive.

To investigate this possibility, samples of authentic polyethylene (PE) and (PVC) films were extracted with water and with solvents, in the same manner as the PVA tape. The results for the  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  analyses are summarised in Fig. 3, with

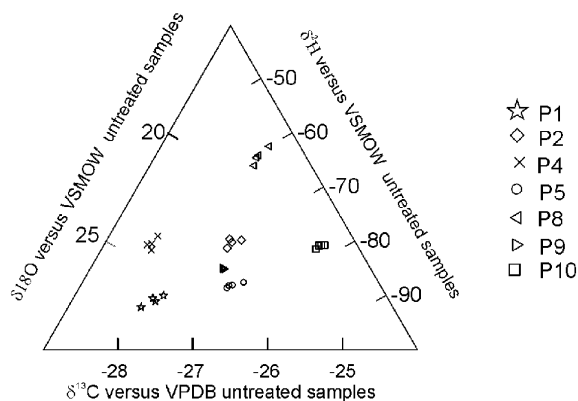


**Fig. 3**  $\delta^{13}\text{C}$  data versus  $\delta^2\text{H}$  data for polyethylene (PE) and poly(vinyl chloride) (PVC) films extracted with water and organic solvents.

95% confidence ellipses presented for the unextracted, water extracted and solvent extracted PE and PVC films. The three ellipses corresponding to the PE film exhibit almost complete overlap, indicating no significant changes during the extraction processes. The unextracted PE film exhibits the widest uncertainty, which may indicate an inhomogeneous surface deposit that was removed by washing. The PVC film, in contrast, undergoes a significant change in isotopic content when extracted with solvent, both  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  becoming enriched in the heavier isotope. GCMS analysis of the solvent extract showed it to contain bis(ethylhexyl)adipate ( $\text{C}_{22}\text{H}_{42}\text{O}_4$ ), a plasticiser commonly added to rigid polymers, such as PVC, to increase flexibility. Smaller quantities of phenolic antioxidants (*e.g.*, *tert*-butylphenol) were also detected. The presence of these compounds will clearly contribute to the measured  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values for the overall polymer film. The solvent extracted PE and PVC films exhibited smaller uncertainties in  $\delta^2\text{H}$  measurements than the unextracted counterparts, a finding which is in contrast to the PSA tape samples. It is possible that this effect is due to the removal of inhomogeneous additives on the surface or within the film.

Figs. 1C and 1D represent the  $\delta^2\text{H}$  data for the untreated and treated PSA tapes as box plots. The deuterium isotopic content spans a much wider overall range than  $\delta^{13}\text{C}$  but provides less discrimination, with seven of the ten samples forming a group with  $\delta^2\text{H}$  values between approximately 75 and 85‰ versus VSMOW. The  $\delta^2\text{H}$  data for the treated samples show approximately the same distribution as the untreated samples, with generally broader data ranges resulting in even less discrimination. The one exception was P8, which became significantly isotopically enriched with smaller variance, which earlier experiments showed to be a characteristic of PVC. Because of the similarity in the box plots, a plot of  $\delta^2\text{H}$  data for untreated versus treated samples (not shown) does not provide an additional means to discriminate the samples. Combining the  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  data for the untreated PSA tape discriminates eight of the ten batches with a high degree of assurance (Fig. 2B). A plot of  $\delta^2\text{H}$  versus  $\delta^{13}\text{C}$  data for the treated samples (Fig. 2C) is less discriminating, due to greater variance in the data, but does identify P5 and P10 as discrete groupings, in contrast to Fig. 2B. A significant number of the samples form a close grouping, again suggesting a common source for the backing material.

Fig. 1E represents the  $\delta^{18}\text{O}$  data for the untreated PSA tapes as a box plot. Samples P3, P6 and P7 do not appear in this plot as they contained no detectable amounts of oxygen, suggesting that the adhesive was natural rubber rather than acrylic. No detectable amounts of oxygen were present in any of the treated tapes, confirming the inference that these samples contained an acrylic adhesive. The seven samples which contained detectable



**Fig. 4** Triangular plot of  $\delta^{13}\text{C}$  versus  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  for untreated samples. (P3, P6 and P7 did not contain analysable amounts of oxygen).

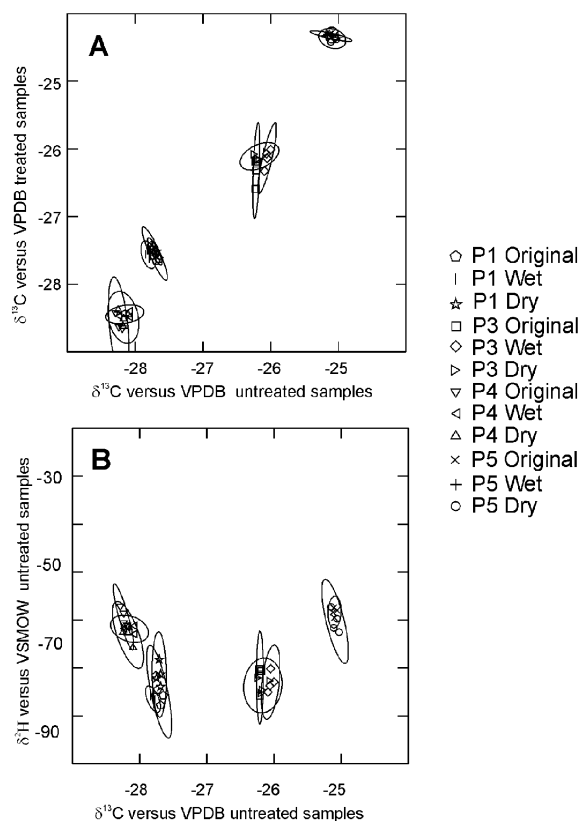
amounts of oxygen formed three groupings and this technique therefore, provided only limited discrimination. The fact that some of the samples do not contain oxygen in itself provides a means of discrimination. The combined  $\delta^2\text{H}$ ,  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data for seven samples of untreated PSA tape are presented as a triangular plot in Fig. 4, the individual groups being readily distinguished. Although samples P2/P5/P9 appear in close proximity, the use of spherical or polar coordinates may be employed to make the differences more apparent.

These initial experiments have shown that the isotopic composition of PSA tape provides many criteria by which to discriminate between batches. A suitable analytical sequence for the comparison of two tapes is summarised in Table 1. The first three analyses are identified as having the greatest ability to discriminate between samples. If, at any stage, the data are divergent then it becomes possible to conclude that two samples do not have a common origin. If the protocol yields parallel results at all stages this provides strong evidence that the two tapes share a common origin. Some care must, however, be exercised when interpreting data from treated tapes, since the solvent extraction process may not remove equivalent material from all samples unless they are analysed in tandem.

To be of genuine forensic use the technique must be able to relate samples of PSA tape to a common origin following a period of use or storage. To assess this potential parcels were prepared to resemble those often used to conceal drugs, as described above. Providing the tape was wound around at least twice, such that the second layer partially covered the first, there was sufficient tape available for analysis. Fig. 5A presents a plot of the  $\delta^{13}\text{C}$  content of the treated versus the untreated PSA tapes. Results for the original tape and for tape taken from the parcels stored under wet and dry conditions are superimposed. For each sample the 95% confidence ellipses corresponding to the three data sets overlap, indicating no significant difference between the original tape and the material

**Table 1** Summary of overall analytical protocol for the comparison of PSA tapes. If, at any step, the data are divergent then it is possible to conclude that two samples do not have a common origin. If the protocol yields parallel results at all stages this provides strong evidence that the two tapes share a common origin

Step 1	<b>Sample intact tape</b>	
Step 2	$\delta^{13}\text{C}$ determination	
Step 3		<b>Remove adhesive layer</b>
Step 4		$\delta^{13}\text{C}$ determination
Step 5	$\delta^2\text{H}$ determination	
Step 6		$\delta^2\text{H}$ determination
Step 7	$\delta^{18}\text{O}$ determination	



**Fig. 5** Plots of  $\delta^{13}\text{C}$  data for untreated versus treated samples (A) and  $\delta^2\text{H}$  data versus  $\delta^{13}\text{C}$  data for untreated samples (B) for original tape and “wet” and “dry” parcels.

removed from the parcels. Fig. 5B presents  $\delta^2\text{H}$  versus  $\delta^{13}\text{C}$  for the untreated PSA tapes and parcel samples. Again, for each sample the 95% confidence ellipses corresponding to the three data sets overlap, indicating no significant differences. Although proton exchange has been shown to occur for most chemical compounds over a sufficiently long timescale,<sup>14</sup> no change in the deuterium content is apparent as a result of proton exchange with the water during this experiment.

## Conclusions

The isotopic analysis of PSA tapes provides a number of parameters by which to determine whether samples belong to a common batch. The technique requires small samples and preparation is rapid and straightforward. Special handling requirements, such as the use of powder free gloves, did not prove necessary.

Basic  $\delta^{13}\text{C}$  analysis of intact PSA tape has the potential to discriminate between a high proportion of samples. Where this measure proves ambiguous, removal of the adhesive layer and subsequent  $\delta^{13}\text{C}$  analysis of the underlying polymer provides a further means of classification. Additional characterisation may be obtained by  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  analysis of the intact tape and by  $\delta^2\text{H}$  analysis of the backing material, although these techniques are experimentally more difficult than  $\delta^{13}\text{C}$  determination.

Short to medium term storage conditions were found not to influence the isotopic content of PSA tape and it is concluded, therefore, that the method has the ability to link samples of PSA tape originating from the same batch following a period of use. The technique has many potential forensic applications in linking material found at different times and locations, crime scenes, premises, etc.

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