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## Stable isotope profiling of burnt wooden safety matches

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# Abstract

Arson is a significant problem around the world, and is a crime which results in a low number of convictions. The scene of an arson can be varied, commercial, residential or national park, and recently cases have been identified which were initiated by a lit match. Matches can be recovered from a scene, usually in a burnt condition. The benefit of analysing unburnt matches has been researched previously[1,2]. In most cases, burnt matches are recovered from scenes, and therefore the research was extended to investigate the potential of using IRMS to analyse burnt matches. This includes samples which have been exposed to petrol, and various fire extinguishing chemicals.

Matches were sectioned to reveal central unburnt portions of wood and analysed by isotope ratio mass spectrometry (IRMS). The stable isotope profile (SIP) of the wooden matchstick samples was unaffected by the presence of both petrol and a variety of fire extinguisher chemicals. Any changes seen could be attributed to the natural variability of isotopic composition encountered in a natural material such as wood. These findings were confirmed by the isotope analysis of 19 matchstick samples placed in mock fire training scenarios. The data was examined using a paired *t*-test and Hotelling's  $T^2$  test for a single sample.

# Introduction

Government statistics show there are an average of 3,600 arson attacks per week in the UK, which results in 2 deaths and 60 injured people. Arson attacks cost the economy 40 million a week in England and Wales. Although the problem is growing, the number of cases where a suspect is identified and either cautioned or charged with an offence was 8% of the total number of arson cases recorded by the police in 2001/20023.

Fire extinguishers are designed and simplified to cover a range of possible scenarios which may be encountered. There are four main types of fire extinguishers which are colour-coded for easy identification by the user: water (red), carbon dioxide (black), dry powder (blue), and foam (cream). Synthetic foams such as aqueous film forming foams (AFFF) consist of alpha olefin sulphonates and/or perfluorooctane sulphonate and perfluorooctanoic acid as surfactants. A powder extinguisher usually contains a sodium bicarbonate based powder and carbon dioxide to expel the powder.

Wooden matches are an item commonly encountered at many scenes of crime. Matches are usually associated with fire scenes, where although unburnt matches are sometimes found at the scene, burnt matches are far more common. Some analytical methods have been used to identify the components of burnt match-heads by energy dispersive x-ray analysis<sup>4</sup>, however, little work has been carried out to date analysing burnt wooden matchsticks within a forensic science context. Microscopy of thin sections has been used to identify the type of wood, however this has its limitations as matches are commonly manufactured from aspen. Some benefit was seen when microscopy and isotope ratio mass spectrometry (IRMS) were combined with x-ray diffraction (XRD) for the analysis of unburnt matches<sup>1</sup>. The aim of this study was to better understand the potential of IRMS as a tool to differentiate burnt wooden matchsticks found at fire scenes. This included burning matches in the presence and absence of petrol and using a range of fire extinguishing materials to extinguish the fires. Fire investigation is a complex process and the causes of fire are numerous. Matches would usually be used to ignite a flammable liquid or fuel. For the purposes of the experiment the effect of the presence of petrol upon the SIP of the match was examined. In addition, fires can also be extinguished in numerous ways. A range of fire extinguishers available in the UK, were obtained and used to extinguish matches burning in the presence of petrol. The method used to extinguish the fire could also influence the SIP of the match, and so a variety of fire extinguishers

available in the UK were used.

Finally to test the robustness of the method, matches were placed in fire scenes used for training purposes. The scenes varied, and were therefore used to fully test the method and test the hypothesis that if matches are sectioned to reveal unburnt portions of wood, the unburnt section could be analysed and the SIP obtained which can be used to identify a potential geographical area of growth and production of the wood, [1,2].

## **Materials and methods**

### **Effect of the presence of petrol and method of extinguishment**

For initial tests a brand called Cooks Matches was used. These are a brand of standard matches approximately 3.8 cm in length, sold in many outlets and supermarkets throughout the UK in boxes of approximately 40. Five Cooks Matches were retained unburnt for comparison and a further five Cooks Matches were burnt using a blowtorch. For each of the following tests a further five matches were placed on a metal sheet, petrol was applied and the matches lit with a blow torch after 5 minutes. The matches were ignited for 30 seconds. The matches were extinguished using a fire blanket. To determine the effect of the four different fire extinguishers, the process was repeated four times with a further five matches in each case. The fire was extinguished with one of four fire extinguishers in turn: water, powder, A-FFF Fluorofoam and CO<sub>2</sub>. These samples were labelled according to the fire extinguisher used to extinguish them.

### **Exposure to compartment fires**

Matches from the same box of Cooks Matches were also placed in a fire scene used for training purposes. Ten matches were placed in two locations in the scene and were la-

belled according to where they were placed in the scene; table and desk. These matches were recovered immediately after the fire was extinguished. It was not always possible to recover all samples for comparison. Three probes placed in the room, by the ceiling, the floor and the centre of the room, were used to record the temperatures to which the matches were exposed. This is indicated on the time temperature graph given in Figure 1. The matches were exposed to the middle temperature which reached approximately 950 C during the fire.

27 boxes of matches of varying brands, available in the UK (with the exception of J11) were purchased from a variety of outlets. These are detailed in Table 1. Ten matches were removed from each box, five were placed in fire scenes used for fire investigation training and the other five retained for comparison. Those matches placed in the scenes were collected (as far as was possible), after the fire was extinguished using water in each case. The samples were arbitrarily labelled J1 to J27, and each was packaged separately. Only 19 of the 27 samples were recovered, the remainder were either consumed in the fire or were too badly burnt to be analysed using the method developed during the course of this work. Three of each of the matches collected from the scenes were used for analysis. Details of the temperatures to which the matches were exposed is indicated on the time temperature graph given in Figure 2. The matches were exposed to the middle temperature which reached approximately 1000C during the fire.

## **Sample preparation**

If petrol was applied to matches prior to burning, petrol additive residues which remain on the match could potentially affect the resultant stable isotope profile. Experiments revealed that the burnt portion of wood gave results which were mainly composed of carbon, due to burning. To produce a representative samples, the unburnt wood was

analysed The matchstick was sectioned to reveal the central unburnt portions of the wood. This was achieved using pristine scalpel blades. The unburnt wood in the centre of the matchstick was removed and stored separately. To confirm this portion of the match remains unaltered, the sample was compared to unburnt samples from the same box. All samples were weighed into capsules and analysed for  $^{13}\text{C}$ ,  $^2\text{H}$  and  $^{18}\text{O}$  isotopic composition as detailed in Farmer et al<sup>1,2</sup>. The isotopic results from each of the burnt matches were compared to the appropriate matched sample from the same box using two tailed t-tests with a 95% confidence interval ( $P < 0.05$ ).

## **Results and Discussion**

### **Effect of petrol on wood**

The range of  $^{13}\text{C}$  isotopic composition for the unburnt matches was found to be 2‰, increasing to a maximum of 4‰ for matches burnt with petrol. No statistically significant difference was found between these samples, therefore this increase could simply be due to the range of up to 6‰ which can be expected in a box of matches. This concurs with previously reported results by Farmer et al [3]. The difference is unlikely to be due to the presence of petrol as most will have either volatilised or burnt, and any additives remaining would have adhered to the outer portion of the match only.

### **Fire Extinguisher Tests**

Initial tests were carried out where matches were burnt and extinguished in a variety of ways and compared to unburnt samples. No statistically significant difference was found in  $^{13}\text{C}$ -values between unburnt samples prepared as described above and any of the corresponding burnt samples. This included samples recovered from the fire scenes. (Figure 2).

Similar to observations made for  $^{13}\text{C}$ , no statistically significant difference was found between the unburnt matches and any of the burnt matches in their  $^{18}\text{O}$  isotopic composition (Figure 3). A range for  $^{18}\text{O}$  isotopic composition of 3‰ was found for the unburnt matches, comparable to those previously reported for inter and intra batch studies [3]. However, the range observed for three sets of burnt matches increased beyond this to a maximum of 5‰. The three sample sets were those burnt with petrol, and those extinguished by water or carbon dioxide extinguishers. The hypothesis initially was the extinguisher had some effect upon the range of the results, and whilst this may be true, a range for  $^{18}\text{O}$  isotopic composition of 4‰ was seen for those matches burnt with petrol and extinguished using a fire blanket. There is no explanation as to why the fire blanket would influence the stable isotope profile of the samples as no additional chemicals are added when extinguishing the fire in this manner. Additionally, those matches extinguished with the foam extinguisher show a considerably smaller range of 2‰. If the use of a fire extinguisher were responsible for the increased range it would be expected that all chemical extinguishers would show an increased range and those extinguished by the blanket would be comparable to the unburnt matches. It is more probable, therefore that a range of up to 7‰ is possible, due to variation within the original tree, as discussed previously in Farmer et al [2].

The  $^2\text{H}$  isotopic composition of the majority of matches extended over a range of 25‰, similar to the results reported in Farmer et al, where an intra-box  $^2\text{H}$  variation of 35‰ for those matches collected from around the world was shown. No statistically significant difference was observed for  $\delta^2\text{H}$ -values between burnt and unburnt matches (Figure 4).

Using the method of sectioning unburnt parts from burnt matchsticks, samples could not be ground prior to analysis due potential loss of sample material when using the freezer mill available in our laboratory. This increases the variability of measured isotope ratios

since the analysed sample material is not homogenous<sup>6</sup>. Increased variability should be taken into account when interpreting the data since it may account for some of the larger ranges in  $\delta$ -values observed during this initial study. The burnt portion of wood could be only be analysed for its  $^{13}\text{C}$  isotopic composition. In order to maximise the potential of the technique, unburnt sections of wood were analysed to enable three-dimensional stable isotope profiles (SIP) to be constructed.

No statistically significant differences were found for  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ - values of burnt and unburnt matches even when petrol was added to the sample and the burning sample was extinguished with a range of fire extinguishers.  $\delta^{13}\text{C}$ -values for 28 petrol samples collected from around the world were found to range from -25 to -33.5‰, and the  $\delta^2\text{H}$ -values range from -60.6 to -145.5‰[5]. Given these ranges for  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ -values of petrol, which are significantly different from the corresponding  $\delta$ -values for the matchstick samples analysed as part of this study with average  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ -values of -24 and -108.5‰, respectively, petrol would be expected to have some effect upon the match sample isotopic composition. This did not occur, thus the variation seen for the matches, especially for  $^2\text{H}$  composition is likely due to natural isotopic variation in wood than attributable to the petrol used to light the samples.

## 0.1 Samples recovered from Fire Scenes

Three matches, each of the same brand, were recovered from the fire scene. Each recovered burnt match was sectioned to reveal the unburnt portion of the wood. This unburnt portion was analysed in triplicate for the  $^{13}\text{C}$ ,  $^{18}\text{O}$  and  $^2\text{H}$  isotopic composition to form a three-dimensional SIP. In addition unburnt controls were collected for comparison to burnt matches. Similarly three matches were selected at random and analysed in triplicate for  $^{13}\text{C}$ ,  $^{18}\text{O}$  and  $^2\text{H}$  isotopic composition. The results for the unburnt and burnt matches were compared using paired two-tailed t-tests at a 95% confidence interval for

each of the nineteen samples.

Samples collected from the fire scenes were analysed for  $^{13}\text{C}$ ,  $^{18}\text{O}$  and  $^2\text{H}$  to form a three-dimensional SIP. The fire scenes are used in fire investigation training and permit a range of conditions and the varying effects of true fires to be studied. One would expect the range of factors that can influence a fire to lead to a high degree of change in isotopic composition. Yet, the range for  $^{13}\text{C}$ ,  $^{18}\text{O}$  and  $^2\text{H}$  isotopic composition for the 19 burnt match samples was no larger than that seen for the burnt matches test and was comparable to those reported in Farmer et al [3] (Figures 7-9).

The range of observed  $\delta$ -values for some of the samples is notably larger in some cases than others, for example  $^2\text{H}$  isotopic composition of J7 compared to J13, and the  $^{18}\text{O}$  isotopic composition of J3 compared to J8. This may be due to intra-batch variability within the box of matches, compounded by the fact that the samples were not ground prior to analysis leading to higher within sample variation<sup>6</sup> or this may be due to variations within the fire scene as the fire progresses. The samples were left open to the atmosphere prior to sectioning to allow volatilisation of organics and stored in an evacuated desiccator prior to analysis. It is therefore unlikely that the observed variation is due to the fire scene. For all 19 samples two-tailed  $t$ -tests indicated that when  $^2\text{H}$ ,  $^{18}\text{O}$  and  $^{13}\text{C}$  isotopic composition are compared for the burnt and unburnt match samples, no statistically significant difference exists between them (Table 3).

To confirm this conclusion further statistics were applied. The three elements can be visualised (Figure 10). This shows the differences between the burnt and unburnt matches, ignoring subject variability, by plotting each of the three replicate measurements as a different result. The data in Figure 10 can be rotated to produce Figure 11. The hypothesis states that there is no difference between the matches. If this were true, the points

would centre around zero. This seems to be the case in Figure 11. Figure 11 also shows that there is a high degree of subject variability as published in Farmer et al [1,2].

A multi-variate analogue of the paired  $t$ -test (Hotellings  $T^2$  for one sample) was applied to the data. The Hotellings  $T^2$  test for one sample has been considered for forensic data previously [7]. A one sample test was used as the hypothesis states there is no difference between unburnt and burnt matches. The one group considered in the test consists of the group of differences.

Each observation was represented as  $y_{ijt} = C_{ijt}, O_{ijt}, H_{ijt}$ , where  $i$  is the match,  $j$  is the repeat measurement for each match, and  $t$  is whether the match is  $u =$  unburnt or  $b =$  burnt. It is not the individual values for burnt and unburnt matches that is important, but rather the differences between the unburned and burned measurements. This gives:

$$d_{ij} = y_{iju} - y_{ijb}$$

The hypothesis is that the SIP of a match does not change in a statistically significant way, and so a burned match may be able to be related back to a box of unburnt matches made from the same source is expressed as versus where is the multivariate population mean difference (i.e. theoretically unknown). This hypothesis was tested using the sample data. Ignoring the subject variability, the Hotellings statistic for a one sample mean is defined as

$$T_0^2 = n\hat{\mu}_d S^{-1} \hat{\mu}_d$$

where  $\hat{\mu}_d$  is the sample mean difference and is defined as:

$$\hat{\mu}_d = \frac{1}{mn} \sum^i \sum^j d_{ij}$$

and  $S$  is the variance/covariance matrix of the differences. It is similar to a simple

$t$ -statistic squared, except that it factors in the correlation between the elements. If  $T_0^2$  is calculated, and  $H_0$  is found to be true,  $T_0^2$  (suitably scaled) should follow a F distribution with  $p$  and  $np$  degrees of freedom where  $p$  is the number of elements ( $p = 3$ ). A F distribution is used with  $p$  and  $np$  degrees of freedom to calculate the  $p$ -value for the hypothesis test, where the scaled statistic is:

$$F_0 = \frac{n - p}{p(n - 1)} t_0^2$$

and the associated  $p$ -value is obtained by calculating  $\Pr(F|F_0); F \sim F_{p,n-p}$ . This gives  $T_0^2 = 2.46; F_0 = 0.79$ , and  $\Pr(F|F_0) = 0.504$ . Therefore, the null hypothesis cannot be rejected, and there is not a statistically significant difference in the SIP due to the burning process.

When a repeated measures model is used, and fitted to the data, the complexity of the statistics increased significantly, and as such only the simpler results have been presented here. However, the conclusions remain the same there is no statistically significant difference in the SIP of the matches due to burning.

## Conclusion

No method for the forensic analysis of burnt wooden matches has been published prior to this work. If microscopy had been carried out on these samples the matchsticks would have been sectioned as reported in this method, to reveal unburnt portions of the matchstick thus revealing merely the type of wood. The isotopic analysis of unburnt wooden portions of a matchstick maximised the information available, producing a three-dimensional profile based upon  $^{13}\text{C}$ ,  $^{18}\text{O}$  and  $^2\text{H}$  isotopic composition as opposed to a one-dimensional isotope analysis, limited to  $^{13}\text{C}$  isotopic composition only if the burnt portion would have been analysed.

An initial study regarding the use of petrol and fire extinguishers found no statistically significant difference when unburnt and burnt matches were compared using two tailed  $t$ -tests. The range of the data was found to increase, probably due to sample inhomogeneity as samples were not ground prior to analysis to avoid contamination.

Burnt samples placed in and retrieved from fire scenes were exposed to conditions expected to occur in real incidents. When the burnt matches were compared to retained unburnt controls of the matches using two-tailed  $t$ -tests, and a multivariate analogue of the paired  $t$ -test (Hotellings  $T^2$  for one sample), there was no statistically significant difference between the samples. These results provide the first indication that analysing matchsticks for geographical origin of the wood they are made of may be possible even for burnt matches, thus yielding additional information especially in case of matchsticks made from the most commonly used wood, aspen [2].

The method developed for the analysis of unburnt matches reported in Farmer et al [4] has been successfully extended to the analysis of burnt matches. This has been demonstrated in both laboratory-based controlled experiments and a variety of real fire training scenes. The method can be used in conjunction with XRD and microscopy methods. The recommendation is that matches should be sectioned prior to analysis to ensure that not petrol residues are adhering to the match surface, thus eliminating any possible error.

## References

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# Figures

Figure 1: Time temperature graph indicating the temperatures the 27 samples in table 1 were exposed to.

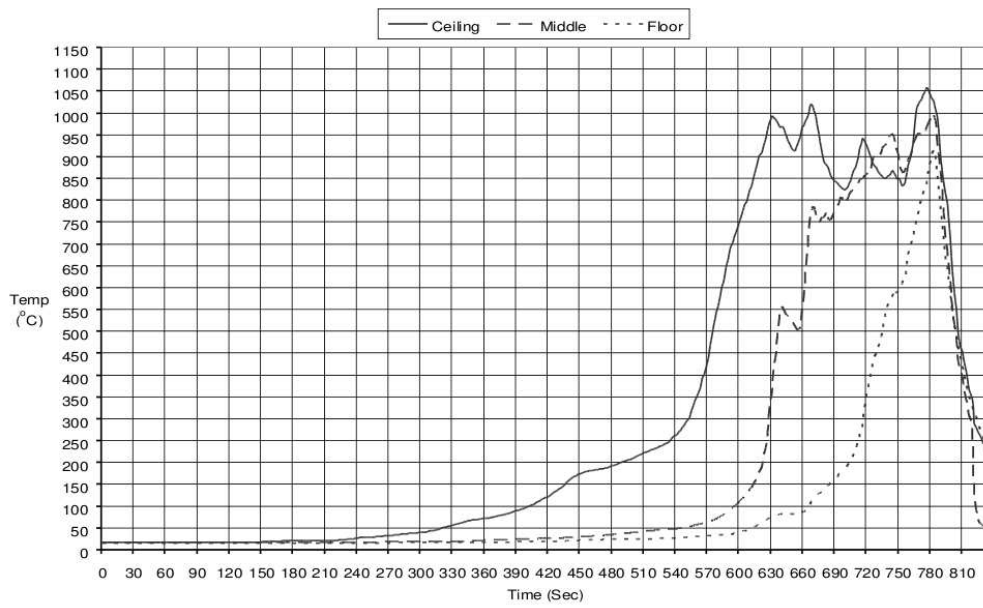


Figure 2: Actually Figures 2,3 and 4 going left to right. Figure 2:  $\delta^{13}\text{C}$  values (‰) for unburnt and burnt matches indifferent scenarios. Values between the inner and outer fences are plotted with asterisks. Figure 3:  $\delta^{18}\text{O}$  values (‰) for unburnt and burnt matches indifferent scenarios. Values between the inner and outer fences are plotted with asterisks. Figure 4:  $\delta^2\text{H}$  values (‰) for unburnt and burnt matches indifferent scenarios. Values between the inner and outer fences are plotted with asterisks. Values beyond the outer fences, called far outside values, are plotted with empty circles.

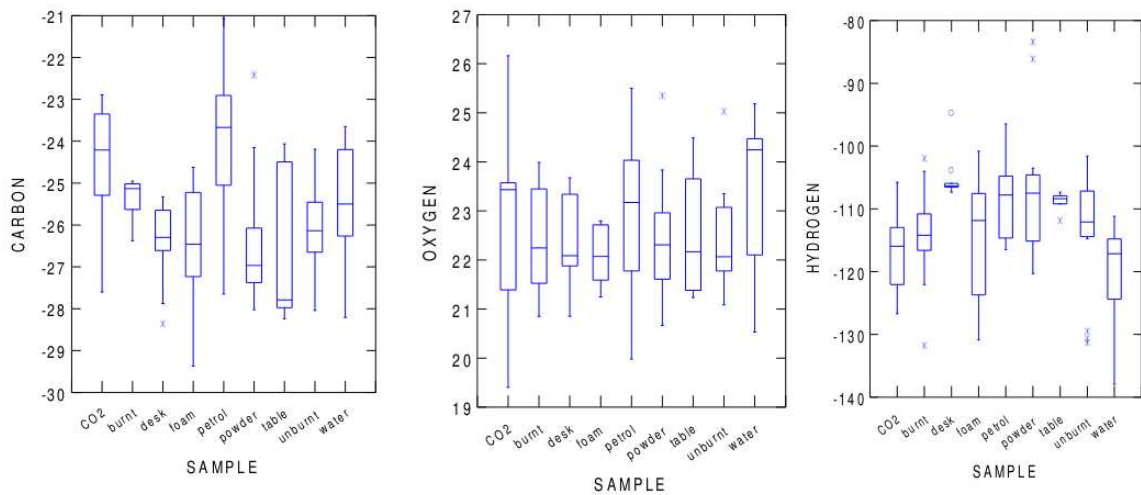


Figure 5: Actually Figures 5 and 6 going left to right. Figure 5 Shows all the data associated with Experiment 1 : Effect of the presence of petrol and method of extinguishment. The samples are represented thus: Bu Burnt, Un Unburnt, Fo Foam, Pe Petrol, Wa Water, CO Carbon Dioxide, Po Powder. There is no noticeable trend to the data, they appear randomly distributed. Figure 6 as Figure 5, but rotated. This shows all the data associated with Experiment 1 : Effect of the presence of petrol and method of extinguishment. The samples are represented thus: Bu Burnt, Un Unburnt, Fo Foam, Pe Petrol, Wa Water, CO Carbon Dioxide, Po Powder. There is no noticeable trend to the data, they appear randomly distributed.

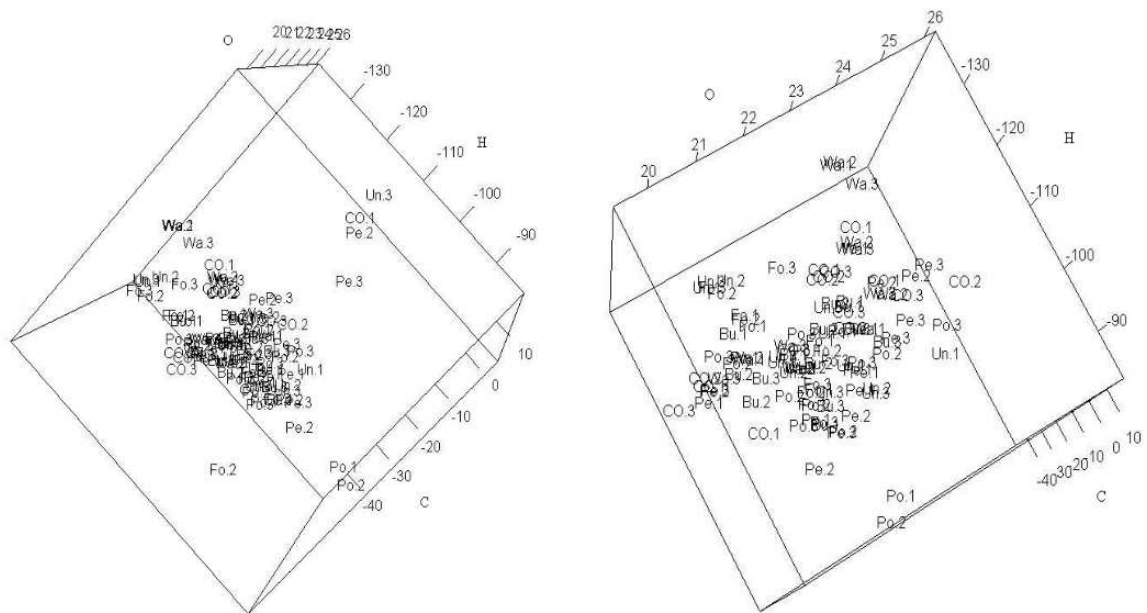


Figure 7: Comparison of  $\delta^{13}\text{C}$  abundance between burnt and unburnt matchsticks selected from nineteen different boxes of safety matches.

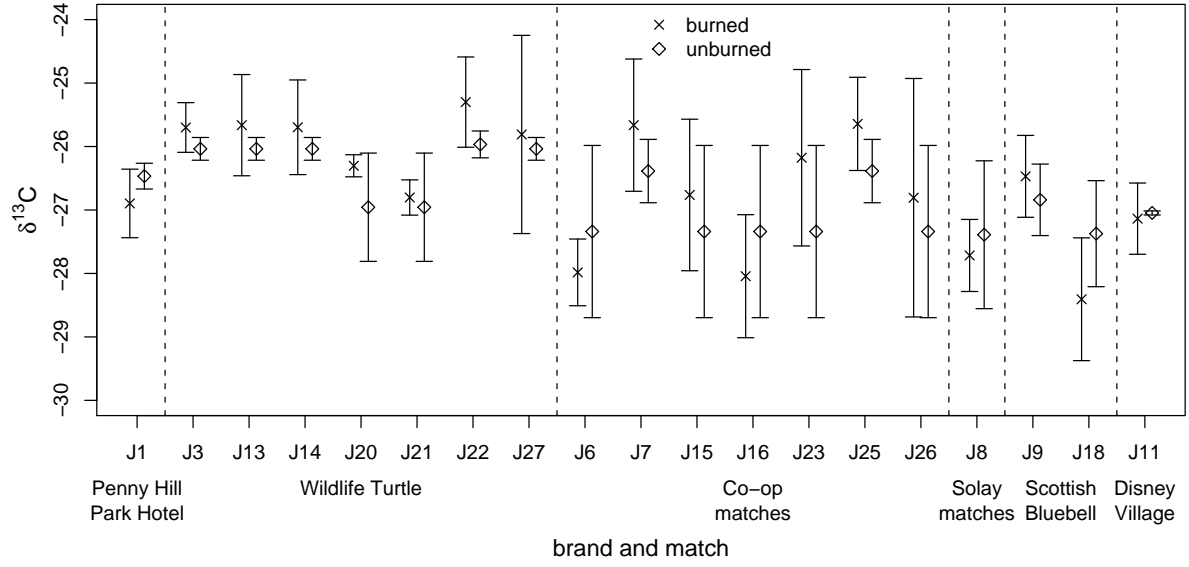


Figure 8: Comparison of  $\delta^{18}\text{O}$  abundance between burnt and unburnt matchsticks selected from nineteen different boxes of safety matches.

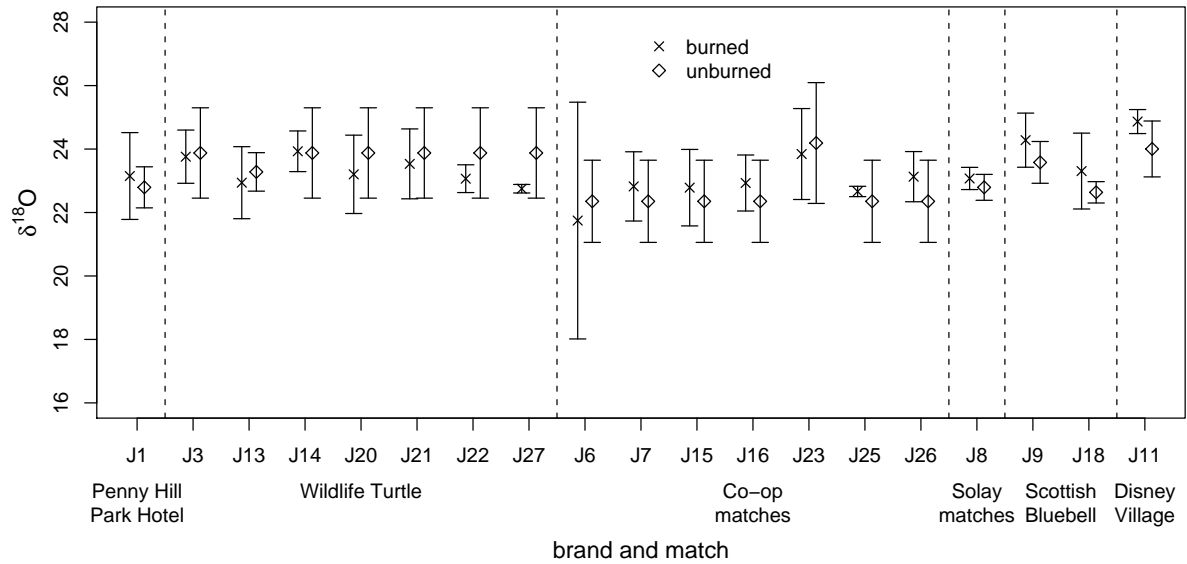


Figure 9: Comparison of  $\delta^2\text{H}$  abundance between burnt and unburnt matchsticks selected from nineteen different boxes of safety matches.

