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TG-MS ANALYSIS OF THE THERMAL DECOMPOSITION OF PIG BONE FOR FORENSIC APPLICATIONS

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In order to investigate the potential of thermal analysis for the determination of post-mortem age, rib bone specimens were collected from the remains of a number of slaughtered pigs that were allowed to decompose in the Australian bush in a controlled site under a range of conditions for time periods ranging from 1 to 5 years. The bone specimens were cut in cross-section with the compact bone collected for analysis. TG-MS curves were collected by heating bone samples to 1100°C in an argon atmosphere. The TG-MS data showed significant differences for the pig bone specimens derived from the different environments and showed trends in peak size correlating with age. The reported data suggest that TG-MS has significant potential for the identification of origin as well as the ageing of skeletal remains in a forensic context.

Keywords: *bone, forensic, mass spectrometry, thermogravimetric analysis*

Introduction

A problem for forensic examiners is the ageing and characterisation of bone fragments or decomposed skeletal remains. The difficulties lie in the complex nature of bone and in its interaction with the environment. Due to the sensitivity of thermal methods to morphological states, thermogravimetric analysis (TG) has been selected as a technique which may overcome these problems.

TG has been utilised for the characterisation of bones in a number of studies [1–7]. TG has also been used in combination with mass spectrometry (MS) to obtain further information regarding the composition of bones [4–6]. The TG data of bones shows mass losses at particular temperatures that may be correlated with the organic and inorganic phases present in bone. The first step occurs from 50–260°C and is associated with water loss. A second step up to 600°C represents the combustion of the organic components to produce carbon dioxide, water and organic fragments. A third step in the range 650–850°C is observed and is associated with the release of carbon dioxide from the carbonated hydroxyapatite if the decomposition is carried out in an air atmosphere, but is predominantly associated with the further decomposition of the products of pyrolysis produced in the second step if the decomposition is carried out in an inert atmosphere [6].

In the current study, TG-MS has been used to characterise bone specimens obtained from pigs of different post-mortem age and subjected to different burial environments. Selected fragments have been monitored in order to find a correlation with post-mortem age.

Experimental

Samples of pig rib bone were provided by the Centre for Forensic Science at the University of Western Australia from the remains of an ongoing research project on the environmental effects of tissue decomposition. Female pigs, 45 kg in weight, were slaughtered and allowed to decompose in the Western Australian bush in a controlled site under a range of conditions which included: burial in a clothed and unclothed state; deposition on the soil surface, also in a clothed and unclothed state; and stored, clothed, in a car purged with carbon monoxide to imitate the decomposition of the pig under the conditions of 'car gas suicide'. The pig carcases were kept in these conditions for a range of time periods from 1 to 5 years. Table 1 summarises the details of the specimens. Rib bone specimens were collected from the remains and cut in cross-section with the compact bone collected for analysis. The compact bone specimens were cleaned only by scaping of the surface with a scalpel

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Table 1 Bone sample details

Sample	Burial conditions	Burial time/year
SC1	clothed, surface deposit	1
SC4	clothed, surface deposit	4
SC5	clothed, surface deposit	5
BU3	unclothed, buried	3
BU4	unclothed, buried	4
BC5	clothed, buried	5
GC1.5	clothed, simulated car suicide by carbon monoxide gas	1.5

Table 2 Total mass loss up to 220, 570 and 1050°C

Sample	Total mass loss/% up to		Final mass loss/% at 1050°C
	220°C	570°C	
SC1	11.5	34.8	43.3
SC4	8.7	33.4	42.1
SC5	8.7	29.8	38.0
BU3	11.5	32.3	41.5
BU4	9.4	29.8	38.4
BC5	10.6	29.9	38.6
GC1.5	8.5	37.9	45.7

to remove fatty bone marrow from the interior and any residues from the exterior of the specimens.

The bone specimens were examined by TG using a Setaram Setsys 16/18 thermobalance coupled with a Balzers ThermoStar mass spectrometer for evolved gas analysis (EGA). Experiments were carried out by placing approximately 15–20 mg of the bone sample into a platinum crucible and heating at a rate of 10°C min^{-1} from ambient temperature to 1100°C under flowing (20 mL min^{-1}) high purity argon gas. Temperature calibration was carried out using indium, tin, aluminium, gold and silver. Baseline curves measured under the same experimental conditions were acquired to account for buoyancy effects on the balance. The mass to charge ratios selected for analysis were 18, 28, 30, 32, 44, 54, 64, 67, 70, 72, 78, 81 and 91 amu. A one second acquisition time for each mass unit was set, thus requiring 0.13 min (or 1.3°C) for each cycle.

Results and discussion

TG and DTG curves for the specimen SC1 are shown in Fig. 1. These curves show the three distinct regions of decomposition; region 1 from room temperature to 220°C, region 2 from 220 to 570°C and region 3 from 570 to 1050°C. Each of these regions is characteristic of a mass loss step, the total mass losses of which are listed in Table 2. The DTG curve is plotted with a selected range of MS mass to charge ratio

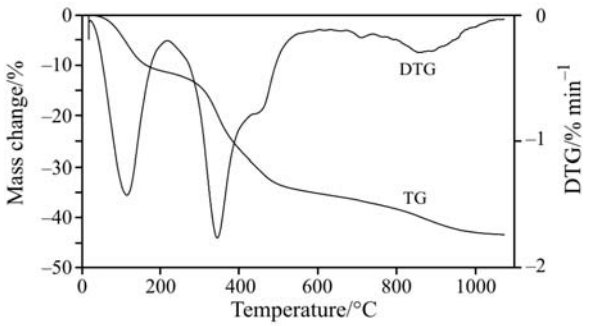

Fig. 1 TG and DTG curves for SC1 bone

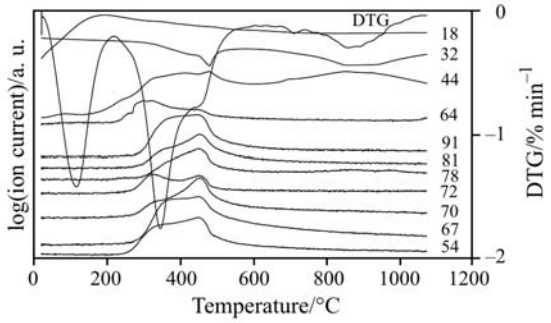

Fig. 2 Temperature dependence of ion current for various fragments of SC1 bone

(in amu) curves in Fig. 2 for the specimen SC1, aiding the characterisation of each mass loss step.

Region 1 is associated with the evolution of water (18 amu) with a peak in the DTG curve observed

at 120°C. The peak in the 18 amu curve is at a higher temperature (190°C). The higher observed temperature may be accounted for by the onset of decomposition processes which evolve water as well as organic species, resulting in a peak shift to higher temperature.

Region 2 is characterised by a two-step decomposition process of the organic material identified with peaks in the MS curves which correspond to organic fragments. The two peaks observed in the DTG are centred on 348 and 451°C in the decomposition of SC1. Inspection of the MS curves in Fig. 2 indicates that there are two types of MS curves attributable to the decomposition of the organic fragments. Of these MS curves, the curves of the 72 and 78 amu mass fragments have been selected for comparison of the range of pig bone specimens listed in Table 1 (Figs 3 and 4). In addition to the organic fragments, CO_2 (44 amu curve) is also observed to be evolved in region 2. CO_2 may be evolved as either a product of the decomposition of the inorganic phase (the carbonated hydroxyapatite) or as a product of pyrolysis. A third possibility is the oxidation of the organic matter by atmospheric O_2. Although the experiments were carried out in an argon atmosphere using high purity argon, the argon purge gas still contains a small amount of oxygen (<10 ppm). It is this oxygen that is likely to be responsible for the CO_2 produced through oxidation of the organic matter. This is supported by the 32 amu curve, attributed to O_2, which is observed to have negative peaks that correspond to the positive peaks in the CO_2 curve. This is confirmed by the presence of a sharp negative peak in the O_2 curve at 483°C which corresponds well with a positive peak at the same temperature in the CO_2 MS curve.

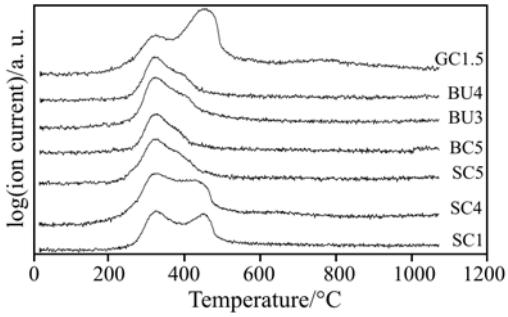

Fig. 3 Temperature dependence of the 72 amu fragment

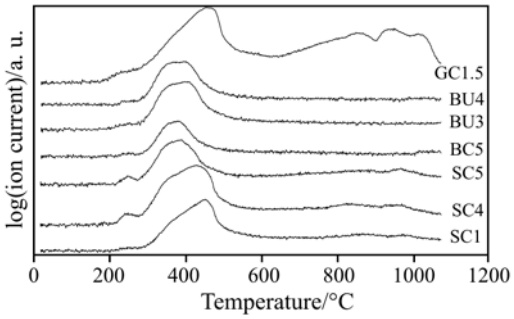

Fig. 4 Temperature dependence of the 78 amu fragment

The thermal decomposition of the specimen SC1 is observed throughout region 3 as the DTG curve is not observed to reach zero even at temperatures above 1000°C. In this region a broad decomposition step is observed from 680 to 1060°C with the peak centred on 875°C. Although there is likely to be some decomposition of the mineral phase in this region, the mass loss appears to be predominantly associated with the evolution of organic products as the O_2 MS curve once again shows a negative peak in line with the positive peak observed in the CO_2 MS curve.

The aim of this work was to apply TG-MS to the characterisation of the series of bone samples listed in Table 1 and to identify the potential of TG-MS as an appropriate tool for the determination of the post mortem age of the bone specimens based on the assumption that as the bone specimens age in situ, chemical change would be observed in the thermal decomposition products in the MS. Additionally, as thermal methods are sensitive to morphology due to the dynamic nature of the data acquisition, differences would be expected to be observed due to a change in the diffusion path length of volatiles produced in the decomposition process, resulting in shifts in mass loss peaks. For this purpose the comparative data are plotted in Figs 3 and 4 for the 72 and 78 amu MS curves, as representative curves of the thermal decomposition of the organic phase, with the DTG curves plotted in Fig. 5.

The DTG curves show some significant variance between specimens which is particularly notable in regions 1 and 2. Five individual decomposition steps can be identified across regions 1 and 2 at 100, 145, 265, 350, 430°C with the first two steps corresponding to region 1 (water loss) and the latter three to region 2 (organic phase pyrolysis). These peaks appear with differing intensities in each of the DTG curves. The specimen GC1.5 is significantly different showing prominent evidence of all five observable peaks. These ob-

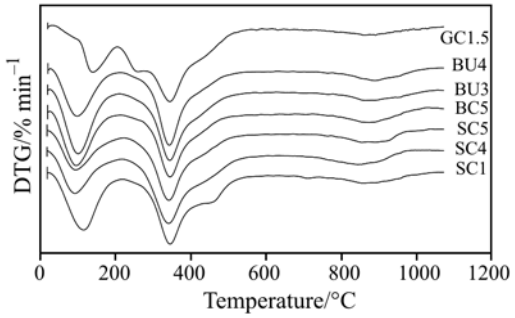

Fig. 5 DTG curves for all bone specimens

served differences might be expected as the decomposition environment of GC1.5 is significantly different; the carcass was sealed in a car which was filled with carbon monoxide and this carcass had no soil contact. The DTG curves of the surface deposited and the buried specimens are more similar, but also have some significant differences in their decomposition character; a peak is observed at 255°C in the 78 amu curves for the SC4 and SC5 specimens, but is absent in the buried specimens' curves (Fig. 4). Although this is a small sample of test specimens, the relatively simple differentiation between the origins demonstrates the sensitivity of TG-MS to origin of the specimens.

Ageing of the specimens by TG-MS also appears promising and certain trends are apparent. The shoulder at approximately 430°C in the DTG curves diminishes in size with increasing age for the SC series. The corresponding peak in the 72 and 78 amu MS curves is also diminished in size for this series. The pair of peaks in the 72 and 78 amu MS curves corresponding to the 350 and 430°C DTG peaks is also indicative of age and appears to be independent of the environment. These are qualitative assessments based on a visual inspection of the shapes of these peaks and, hence, a more rigorous, quantitative study needs to be undertaken with a wider range of specimens for the confirmation of these trends. However, the observation that TG-MS appears to be sensitive to both age and environment should encourage further investigation into the application of this technique to the ageing and identification of the origin of skeletal remains in a forensic context.

Conclusions

A preliminary study has been carried out to identify the potential of TG-MS for the determination of origin and age of skeletal remains. The investigation has identified significant differences between data based on origin and has indicated that ageing trends do appear in the data. TG-MS has, therefore, shown the potential and deserves further investigation.

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