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Guided by Light
The swift characterisation of ancient organic matter by FTIR, IR-fingerprinting and hierarchical cluster analysis.

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This paper presents a method for the swift and approximate characterisation of ancient organic materials. It is an application of Fourier Transform Infrared Spectrometry and fingerprinting comparisons of spectra by correlation coefficients, evaluated through hierarchical cluster analysis. The paper shows that it is possible to make general categorisations using the method, and that the application of statistical methods facilitates the interpretation of old and ancient samples.

Introduction

Partly carbonised, or otherwise preserved, organic matter is often amorphous in character. In these cases, there are few or no visible morphological features to be found and used for identification, and evidence of the original nature of the material can only be provided through chemical analyses. The thorough analysis of organic material from archaeological contexts is a complicated procedure, often demanding cumbersome laboratory work and the use of advanced analytical equipment. However, with the development of new techniques the results obtained are now often astounding. It is today possible to address archaeological problems, using these techniques, that archaeologists ten or twenty years ago only dreamt of solving.

As samples investigated may have a wide range of possible origins, and different materials require different methods of analysis, it is often hard to decide which techniques to apply. It has therefore been of importance to find a quick way to characterise archaeological organic matter. A test method has been required, able to function using very small sample amounts, for use before more detailed analyses.

Organic material

Organic residues may be found in a variety of archaeological contexts. They may be isolated finds in layers or in the fill of features, or they may be found adhering to other artefacts. The archaeological context in itself may contain clues as to the nature of the organic residue. But these assumptions may lead to false conclusions. An example is the term food-crust, often used for organic residues adhering to pottery. On several occasions these residues have proved to have little to do with food when analysed (Isaksson 1997, Olander 1999). It is much better to confirm the nature of the organic residue, and allow the results to provide clues as to the activities of the site, the utilisation of natural resources and so forth.

There are six major natural categories that make up possible origins for archaeological organic materials, i. e. food, bituminous or resinous materials, waxes, oils and fats, carbohydrates, and proteinaceous materials. Food residues, originally containing edible carbohydrates, proteins and fats as major constituents, form a vast group that may be a possible origin of organic residues. Tars, pitches and resins, which also may have been mixed with waxes and fats, form another group. These products may have been used for multiple purposes, e. g. as adhesives, coatings or disinfectants. Waxes are another group of compounds often used as adhesives and coatings, as well as for modelling, as casting material, and in candles. Oils and fats found their use as illuminants, were base for perfumes and in ointments for medical and cosmetic purposes. Drying oils are important as coatings and as binders in paint. Carbohydrates are found in wood, paper, plant fibres, and have also been used as adhesives and binding media. Proteins are found in skin, leather, silk, wool and sinews. Also these materials have been used as binding media and adhesives. The chemistry and analysis of many of these materials in museum objects has been reviewed by John Mills and Raymond White (1994).

The possibilities for the survival of these different materials vary. Two important factors affecting potential preservation are water-solvability and chemical

reactivity of functional groups. Water-soluble material is less likely to survive than insoluble material. Thus carbohydrates and proteins are more likely to disappear completely than are tars, pitches, fats and waxes. Functional groups and chemical linkages vary in reactivity. Consequently, polar lipids and unsaturated fatty acids are, for example, more prone to decomposition than are neutral lipids and saturated fatty acids. Another important determinant in preservation is the immediate burial environment, i. e. mean-temperature, height of the water-table, acidity, aeration and composition, stability and porosity of the soil.

Microorganisms perform the most hasty and devastating decomposition. Materials somehow entrapped, containing a disinfecting capability or deposited in an environment hostile to microorganisms, stand greater chances of survival. Entrapment may occur through incrustation into mineral crusts, such as clay, or corrosion, or through carbonisation. Material entrapped in copper-corrosion has been proved to survive very well (Isaksson 1996:45ff). This may partly be due to the fact that copper-ions quell the growth of many bacteria. Carbonisation, either through heat (Evans 1990:8, Heron & Evershed 1993:253) or fermentation (Slytå & Arrhenius 1979:18ff), generates vesicles within which some of the original material, only slightly degraded, can be trapped. This micro encapsulation into carbonised material inhibit the access of microorganisms capable of degrading organic matter. The heat-treatment result in polymerisation of organic compounds forming more or less inert walls. Other effects are cyclisation, etoxy- and oxo-group formation (Artman & Alexander 1968:643–648). These may also help in preservation, as some of these compounds may be harmful to some microorganisms. Tars and pitches are virtually insoluble in water and several of the compounds in these materials are strong disinfectants. Their chance of survival is therefore considerable.

Method

It was obvious that a method that answered to the qualitative nature of the prerequisites stated above was to be sought within the field of spectrometry. There were some difficulties, however. Several of these techniques require quite a lot of sample preparation and they are all at their most powerful when dealing with chemically homogenous materials.

Biological materials are often chemically complex mixtures, and ancient materials are even worse due to decomposition. However, one of the spectrometric methods had undergone something of a renaissance in the last few decades, infrared (IR) spectrometry, and this appeared promising. This is today one of the more powerful analytical tools used in organic and analytical chemistry. The method utilises the phenomenon that IR-light in wavelengths of c. 2–20 µm, or wave numbers of c. 5000–500 cm^{-1}, is absorbed by chemical bonds and functional groups in organic substances. As these absorptions are characteristic for varying organic molecules they can be used to positively identify the compounds.

Modern IR-spectrometry is performed as Fourier Transform IR-spectrometry (FTIR). In FTIR the light from the IR-source is encoded by a Michelson Interferometer. The measurement result in an interferogram, which is converted into a single-beam spectrum through a complex mathematical computation; the Fourier transform.

One of the leading advantages of FTIR, in comparison with older techniques, is that all wavelengths are measured simultaneously and during the whole measurement-time. Other improvements are the higher amount of energy that reaches the detector, which results in a higher signal-to-noise ratio, and the usually short measurement-time. Taken together, these characteristics lead to large benefits, making it possible to obtain good spectra from very small samples. The sample preparations needed are also minute. So, being swift and managing small sample amounts, FTIR seemed a suitable method for archaeological organic samples.

The IR-spectrum is a graph with wave number on the x-axis and absorbance on the y-axis. Each peak in the spectrum represents a chemical bond or a functional group. The greater the number of compounds in a sample the more difficult it is to extract single compounds from the whole. Archaeological samples are often very complex mixtures. This results in so many absorption bands that these often overlap to the point of yielding only broad envelopes of adsorption with few distinctive features. There are some ways to deal with this problem by separating different constituents prior to IR-analysis. One way to do this is by preparative separation, for example by a suitable thin-layer chromatography (TLC) system; another is through solid phase extraction (SPE) and a third by selective extraction. However none of these methods was particularly tempting because a quick and non-laborious technique was sought. Another way to tackle the problem is to let the spectrum serve as a chemical fingerprint. To identify an unknown sample, one need to compare its IR-spectrum with a set of standard spectra recorded under identical conditions. Samples that give the same spectra are identical.

This is a very strong proof of identity. For two spectra to be really identical involves recording the spectra on the same machine under identical conditions of sampling, scan speed, resolution etc. The task of comparing spectra is one very suitable for computers. However, a computer library search could never provide reliable proof of identity for a new unknown sample. At best, one would obtain stored spectra which have similar features to those of the unknown. The analyst then has to interpret this information in combina-

tion with other data before the identity of the unknown sample can be deduced (Kemp 1991:55–56).

At the Archaeological Research Laboratory, Stockholm University, reference databases containing spectra of materials of interest are being built up. These include fresh, but mostly experimentally decomposed modern material, and old and ancient materials of known origin. It is important to decompose or better to use ancients samples as diagenesis generates decomposition products, increasing the complexity of the material, leading to a general blurring of spectra (Mills & White 1994:21). A methodological hypothesis of this study is that even-though the spectra of ancient samples may be blurred and contain mostly broad bands of adsorption, the appearance of the spectra depend more strongly on general categories of origin than on any other factor. That is of course generally speaking. Extreme treatments, like exposure to very high temperatures in the past, or extreme burial environments, like in tropic regions, may of course erase all diagnostic features of a sample.

The instrument used in this study was an ATI Mattson Genesis FTIR. It was set to measure between 400 and 4000 cm^{-1}, with a resolution of 4.0 cm^{-1}. The number of scans was 128, yielding a total measurement-time of 2.79 minutes per sample.

The dry samples were mixed with potassium bromide (KBr) to concentrations of 1.0 – 0.2% (weight %). For several sample-types the 1.0%-level was found to be too large, resulting in unclear KBr-pellets. At a concentration of 0.5% most sample-types produced clear pellets and good spectra. Of the sample and KBr-mixture, pellets were produced with a Qwick Handi-Press. Available pellet diameters were 7, 3 and 1 mm. For the 1 mm pellet 3 mg KBr is required, which defines the smallest sample size as 15 µg. For all cases in this study the 3 mm pellet was used, requiring a sample amount of 0.1 mg.

The small sample amounts have several advantages and some risks. One advantage is that I have sample enough to proceed with other analyses after the FTIR-analysis. Another benefit is that small pieces of differing nature in a sample may be extracted under a microscope and analysed separately. An obvious risk with small samples is the peril of contamination. A small speck of dust may ruin an analysis. This can only be avoided through care in the laboratory. Another pitfall is the question of representativity. The composition of a small sample must represent the composition of the whole material. This can to some extent be achieved by homogenising the sample through grinding.

After registering a large number of spectra from different products the task was now to evaluate the resolution of the analysis. To do this spectra needed to be compared and structured. For the comparison of spectra the WinFIRST software was used. The search method uses a specified algorithm to perform an arithmetric data-point-by-data-point search. The algorithm selected for this investigation was the correlation coefficient option. This algorithm is a linear regression. As such, it can account for factors such as baseline drift, differences in scaling and so on. No data pre-processing, such as baseline correction or normalisation, is needed. Also, because the calculated match values are correlation coefficients, the search results are not a measure of relative best fit, but are instead absolute values with statistical significance. The correlation coefficient was calculated by the formula:

$$M = [\Sigma x_i y_i - ((\Sigma x_i \times \Sigma y_i)/N)]/[(\Sigma x_i^2 - ((\Sigma x_i \times \Sigma x_i)/N) \times (\Sigma y_i^2 - ((\Sigma y_i \times \Sigma y_i)/N)]^{1/2}$$

where M = calculated match value (correlation coefficient), and x_i and y_i = ordinate values at *i*th abscissa value of library spectrum and sample spectrum, respectively.

It is unlikely that dissimilar compounds in the library will display correlation coefficients higher than 0.95. To explore the value of the spectral libraries it was important to inquire if the data produced were organised into meaningful structures. For this purpose hierarchical cluster analysis was applied, a statistical method that may be used to test hypotheses of groupings. The method provides an indication of group structure rather than a rigid model of the data (Bratchell 1989:106, 125).

By comparing spectra in the WinFIRST spectral libraries with one another, a correlation of each sample to all others was obtained. This data was transferred to Microsoft Excel and arranged into a correlation matrix. The matrix was then transferred to the STATISTICA software package. The correlation matrix contains measures of similarity which had to be converted to dissimilarity, or distance. The correlation matrix was thus converted to a distance matrix, computed as 1.0-Pearson r. The hierarchical cluster method uses these distances to form a tree diagram. The linkage rule used was the UPGMA (unweighted pair-group method using arithmetric averages) (Sneath & Sokal 1973). This method calculates the distance between two clusters as the average distance between all pairs of spectra in two different clusters. It was chosen as it is very efficient when the objects form naturally distinct groups, but performs equally well with elongated chain-type clusters. The correlation coefficient is not generally considered to be an ultimate measure of similarity between objects (Bratchell 1989:113), but other techniques of comparing spectra would have demanded baseline corrections or normalisation of spectra. All such data processing is a manipulation of raw data, and I wanted to avoid that.

A problem with cluster analysis is that there is no common rule to define a cluster through any precise mathematical definition. However, humans have a remarkable capacity for visually recognising patterns,

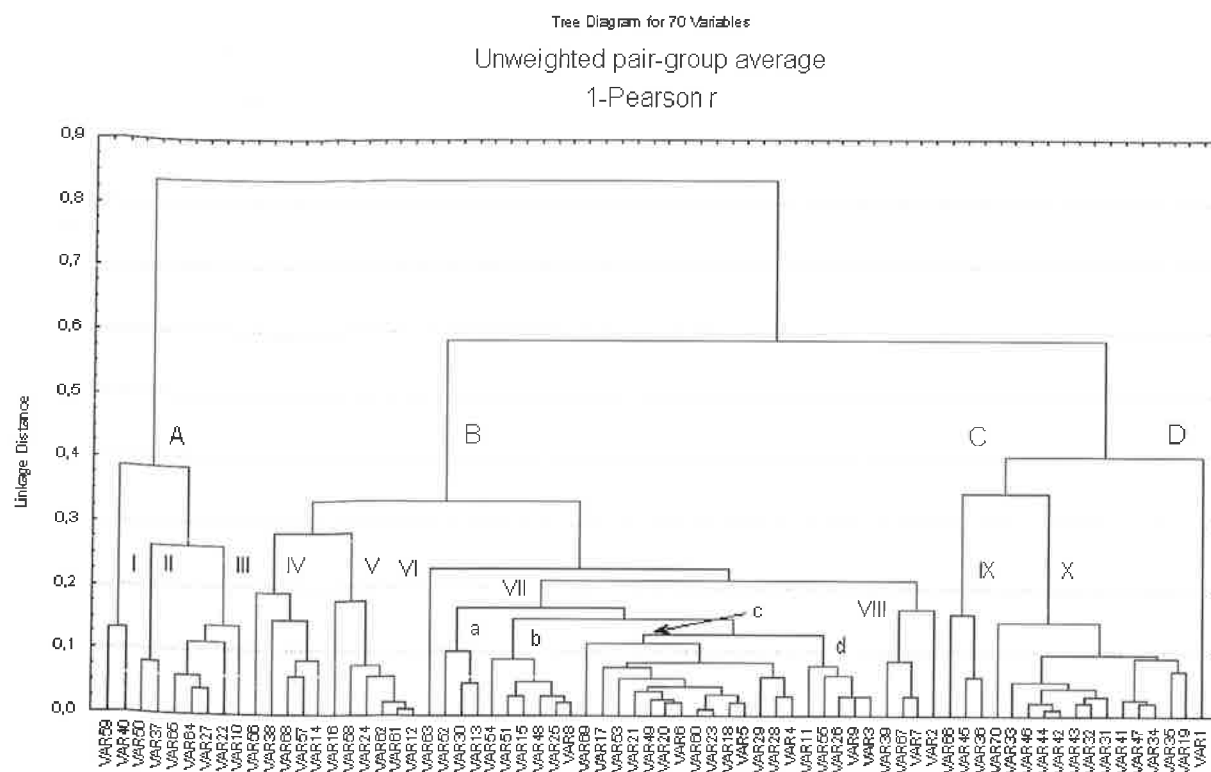

Figure 1a. Tree diagram, based on the correlation coefficient matrix of the 70 samples.

which is so far unmatched by mathematical techniques (Bratchell 1989:108). In this study all samples are of known origin, and I will simply investigate to what level the data is sensibly structured. An aid in deciding the number of clusters is the graph of amalgamation schedule. This is a line graph of the linkage distance at successive clustering steps.

A clear plateau in this graph means that many clusters were formed at similar linkage distances which may indicate an optimal level of defining clusters. A clear cut-off point, where the line begins to rise steeply, may be helpful in a similar way. At such a point the distances between clusters increase rapidly, and so does the within-cluster diversity. But one cannot rely solely on the tree diagram for the interpretation of unknown samples. The spectra has to be scrutinised, and bands of absorption explained.

Samples

Of the hundreds of samples and references of all sorts that have been analysed at the Archaeological Research Laboratory, a set of samples were selected for this study. One aim in the selection was to get both ancient (prehistoric), old (medieval and historic), modern and experimentally decomposed material of indisputably known origin. The origin of old and ancient samples has been established by other methods, such as botanical or thorough chemical analysis. The samples were also selected to mirror as many of the materials mentioned above as possible, with a North European prehistoric context in mind. Altogether 70 samples were selected, presented in detail in table 1.

Results

The hierarchical cluster analysis of the 70 IR-spectra resulted in four major clusters, A, B, C and D (fig 1a, table 1). All form at a linkage distance of about 0.4, which is a bit above the cut-off point of the line graph (fig 1b). All clusters except D consist of a number of sub-clusters, I–X. They form at a linkage distance just under 0.2, which roughly represents the cut-off point (fig 1a and b, table 1). The four large clusters reflect broad similarities in the IR-spectra of their individual members. Cluster A contains samples that have been exposed to severe heat and samples rich in fat. The samples in cluster B are all sorts of food and collagenous materials. In cluster C are bituminous (tars, pitches) and resinous materials. Cluster D consists of only one sample, beeswax.

Tight clusters indicate strong similarities in the IR-spectra of the samples, and loose linkages signify a lower degree of correlations. The three sub-clusters in A are quite loosely linked to each other. Sub-cluster I contains two samples of vegetable material strongly degraded by heat. Sub-cluster II contains strongly heat-degraded meat and a 17th century carbonised cereal.

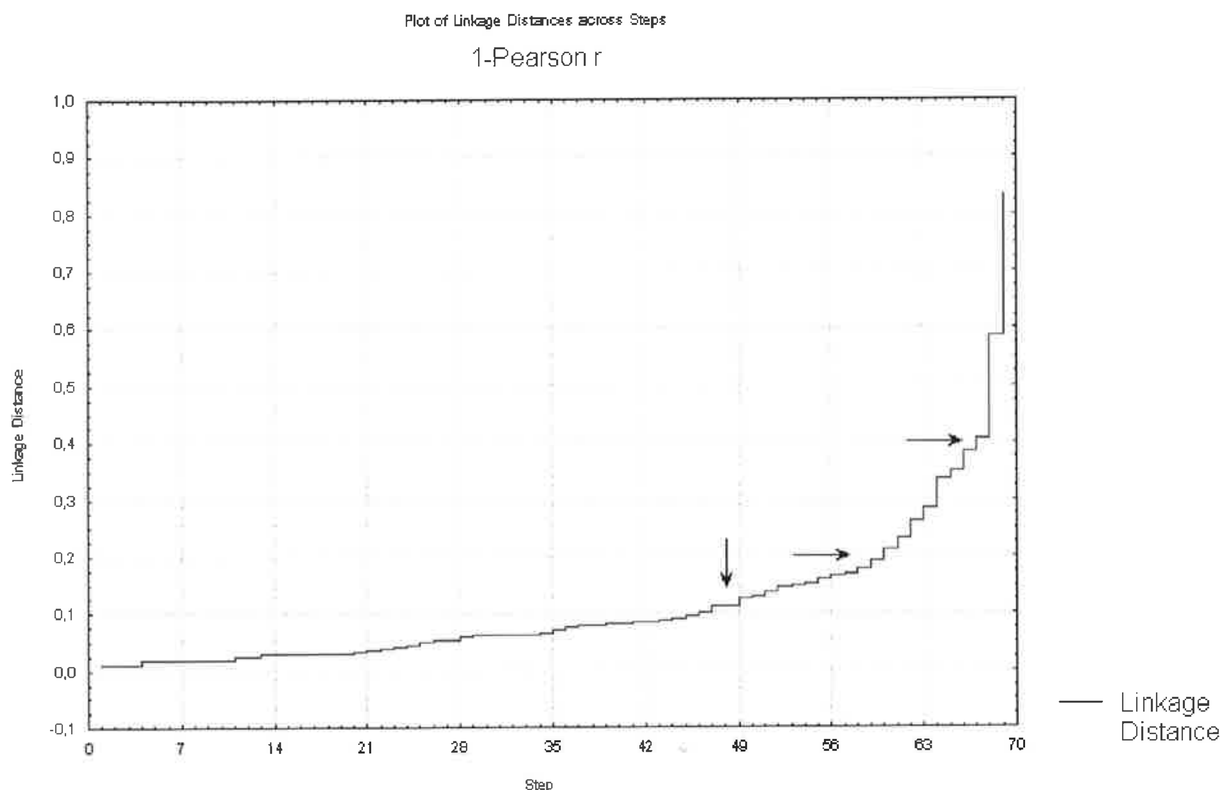

Figure 1b. Graph of amalgamation schedule. Marked points are mentioned in the text.

Sub-cluster III contains mainly oils and fats from different mammals, also degraded cheese, which is rich in fat as well. The spectra in sub-cluster I and II are signified by few and very broad bands of absorption, as a result of the heat-treatment. Sub-cluster III is signified by strong absorption between 2800 and 3000 cm^{-1}. This absorption comes from the acylic chain of the lipids, constituating the fats and oils. Other characteristics are an absorbance-peak at 1730 cm^{-1} and another at 1180 cm^{-1}, which both disclose the presence of ester-bonds, also deriving from the lipids.

Cluster B contains five sub-clusters, of which two are more loosely linked than the others. Sub-cluster VII may be divided further into four minor clusters that are meaningful. These secondary sub-clusters form at a linkage distance of about 0.1, which roughly represents the end of the plateau in the line graph (fig 1b). Sub-cluster IV contains old and ancient vegetable samples. Sub-cluster V contains old, ancient and modern proteinaceous samples. Sub-cluster VI contains only one sample, which is a mixture of a glue made from moose-sinew and tar from birch-bark. This is definitely not food, but the high protein-content of the glue probably draws this sample toward the food. It is however quite loosely linked to the other sub-clusters of cluster B. Sub-cluster VII is a definite food-cluster. It may be further divided into secondary sub-clusters a, b, c and d (fig 1a), were a contains three samples of experimentally decomposed vegetables, b contains experimentally decomposed meat, c contains a second set of experimentally decomposed vegetables and an ancient sample of vegetable-containing material, and d contains four samples of experimentally decomposed vegetables and an experimentally decomposed sample of fish-meat. Sub-cluster VIII contains three ancient or old vegetable samples and one experimentally decomposed sample of blood-bread (Sw. *palt*). Almost all the spectra in cluster B are distinguished by an intense and broad absorbance-peak or envelope of peaks at about 3400 cm^{-1}. This reflects the prominent presence of O-H and O-N bonds in the material. The O-H bond indicates carbohydrates and the O-N bond proteins. The materials rich in carbohydrates also show a strong and often quite broad peak around 1000 cm^{-1} deriving from C-O bonds. The protein-rich materials show a very strong peak at 1650 cm^{-1} and a lower peak or envelope of peaks between 1490 and 1350 cm^{-1}, deriving from N-H and C-N bonds respectively. The band of peaks at 3000-2800 cm^{-1} vary in these samples, and this may reflect a variation in fat content.

The two sub-clusters of cluster C are also loosely linked. Sub-cluster IX contains three quite loosely linked samples of spruce- and pine-resin mixed with fat and a sample of bone-, hoof- and marrow-fat from moose. Sub-cluster X contains a wide range of modern bituminous and resinous materials and one ancient

sample of birch-bark pitch. The spectra in cluster C are mainly characterised by three distinguished features. There are two strong peaks in all samples, one centring at about 2900 cm^{-1} and the other at about 1700 cm^{-1}. There is also a lower and broader peak at about 3400 cm^{-1}. The absorptions derive from the C-H, C=O and O-H bonds of the terpenoid resin acids that dominate these materials. Even-though there are similarities in the absorption pattern of the cluster C materials and the fats and oils in sub-cluster III, the separation is satisfactory. The only mix-up is in cluster IX where one fat-sample shows together with two resin-samples, but this can be explained by the fact that these have been heavily mixed with fat.

The last cluster, D, contains only one sample, beeswax. It is most closely linked to cluster C, and several of the bituminous and resinous samples of this cluster are mixed with beeswax. The sample has its largest set of peaks at 3000-2800 cm^{-1}, deriving from the C-H bonds of acyl-chains in the wax. An absorption band centring at 1468 cm^{-1} derives from the same bonds. Other characteristics are two close peaks at 1736 and 1711 cm^{-1}, produced by C=O bonds in esters and carboxylic acids respectively. A low and broad absorption band between 3600 and 3300 cm^{-1} shows the presence of O-H bonds, deriving from hydroxy-groups in the wax.

Discussion

The applied method was swift and easy, with a minimum of sample preparation. With some practice it was effortless to run some 40 samples in a day. It was possible to get reliable data from as small a sample as 0.1 mg. The actual measurement took little less than three minutes for each sample. All with high-quality spectra.

When IR-spectra of modern, old, ancient and experimentally decomposed organic materials are compared through hierarchical cluster analysis of correlation coefficients, the resulting groupings generally correspond to the natural categories that this analysis sought to separate. Clear differences were discovered in the IR-spectra of highly heat-decomposed material, fats and oils, vegetable and animal foodstuffs, bituminous and resinous materials, and wax. The use of correlation coefficients in the hierarchical cluster analysis, as a measure of similarity between the samples, proved adequate for the intentions of this analysis. When defining clusters the investigation of plateau's and cut-off points in the graph of amalgamation schedule greatly aided the interpretation of the tree diagram.

There are differences between the old and ancient samples on one hand and the modern and experimentally decomposed samples on the other. The old and ancient samples show fewer and broader absorption-bands in their spectra, as a result of further decomposition. The one group with only old and ancient samples on the sub-cluster level, i. e. sub-cluster IV, proves the point. The experimentally decomposed material used in this study has only been exposed to quickened thermal and oxidative degradation. The method of degrading organic matter in the laboratory clearly needs improvement, if higher precision is required. But for general categories the methodological hypothesis of this paper seems to have been corroborated.

The information in the IR-spectra confirms that, viewed using this method, the old and ancient samples bore more resemblance to the materials of which they were originally formed, than they did to anything else. The one exception is sample 37, carbonised hulled barley from the 17th century, which was grouped with severely heated modern references samples. It is therefore probable that this sample has been exposed to high enough temperatures to destroy most diagnostic features. If so, the applied technique may be used to pick out bad samples prior to more cumbersome laboratory work. The experimentally decomposed samples show great differences between exposure to 200°C and 300°C. The later show no or only small absorption-bands in the 1000 and 1700 cm^{-1}-regions, reflecting the loss of oxygenated compounds. This is in accordance with earlier observations on the effects of heat-exposure of organic materials (Johnson et al. 1988:408).

Old and ancient samples of known origin are still the best reference material for the characterisation of unknowns, especially for fingerprint searching in reference libraries. This study shows, however, that modern and experimentally decomposed material can be used to generally categorise ancient organic matter, provided that the unknown sample is correlated to a large set of references of different character and the result is analysed by hierarchical cluster analysis.

Several of the samples analysed did not have a correlation coefficient equal to or higher than 0.95 with any of the other samples. To submit an interpretation at such a point would be very risky. In the cluster analysis the samples gathered in correct categories. There is only one out of 70 samples, or 1.4%, that is erroneously categorised on the secondary sub-cluster level. That is sample 55, cod meat, in secondary sub-cluster VIId which otherwise contains vegetables. All the vegetables in this cluster are rich in proteins, between 11 and 40 percent of the dry-weight. But the vegetables are also rich in carbohydrates, something that distinguish them from the cod. Comparing the cod-sample 55 with the other cod-sample 54, the main difference is in a broad absorption band at about 1300-950 cm-1 in sample 55. A difference in treatment of the samples is that sample 55 was ministered with the strong oxidising agent hydrogen peroxide. The absorption in sample 55 mentioned probably derive from C-O bonds, introduced by the oxidising agent. Other meat-products did not show the

same dramatic effect when treated with hydrogen peroxide. This corroborates the assumption that factors other than chemical structure control the degradative rate of biological material (Harvey & Macko 1997:136-137). Potential factors are the varying presence of preserving compounds and different incorporation in the cellular matrix of the same compound in different tissue.

Even when an unknown is clearly clustered with known references of one category and clearly separated from all others, its make up would usually have to be confirmed using other analytical methods. But from the FTIR-analysis and the statistical evaluation an idea is gained of what to look for, which was the purpose of this paper, i. e. to present a method for the swift and approximate characterisation of ancient organic matter.

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Table 1. Description of the samples

Sample	Description	Cluster
1	Beeswax. Untreated.	D.
2	Blood-bread (Sw. *palt*) on rye and blood. Carbonised beneath a hearth. Produced by Karin Viklund.	B.VIII
3	Broad bean (*Vicia faba*). Carbonised at 200°C for two hours.	B.VII.d
4	Sugar (glucose). Carbonised at 200°C for two hours.	B.VII.c
5	Acorn (*Quercus robur*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.c
6	Juniper berry (*Juniperus communis*). Carbonised at 200°C for two hours.	B.VII.c
7	Carbonised prehistoric rye (*Secale cereale*). Provided by Ann-Marie Hansson.	B.VIII
8	Meat from pig (*Sus scrofa*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.b
9	Grey pea (*Pisum sativum arvense*). Carbonised at 200°C for two hours.	B.VII.d
10	Oil, thermally extracted from adipose tissue of badger (*Meles meles*). Produced by Håkan Strotz.	A.III
11	Vegetable broth powder. Carbonised at 200°C for two hours.	B.VII.d
12	Glue from perch (*Perca fluviatilis*) and pike (Esox lucius) skin. Produced by Håkan Strotz.	B.V
13	Hazelnut (*Corylus avellana*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.a
14	Carbonised oats (*Avena sativa*). Late 13th century. Provided by Kerstin Griffin.	B.IV
15	Meat from lamb (*Ovis aries*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.b
16	Glue from salmon (*Salmo salar*) skin. Treated with acetic acid. Produced by Håkan Strotz.	B.V
17	Linseed (*Linum usitatissimum*). Carbonised at 200°C for two hours.	B.VII.c
18	Root from Lotus (*Nelumbo* sp.). Carbonised at 200°C for two hours.	B.VII.c
19	Viking Age pitch from Lovö, Uppland, made from birch-bark (Sandelin 1998).	C.X
20	Seeds from Alpine Bistort (*Bistorata vivipara*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.c
21	Root from Alpine Bistort (*Bistorata vivipara*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.c
22	Cheese from cow (*Bos taurus*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	A.III
23	Root from parsnips (*Pastinaca sativa*). Carbonised at 200°C for two hours.	B.VII.c
24	Medieval leather from Lödöse, Västergötland, (Mattsson, manuscript)	B.V
25	Dried meat from reindeer (*Rangifer tarandus*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.b
26	Crispbread baked on rye (*Secale cereale*). Carbonised at 200°C for two hours.	B.VII.d
27	Tallow from roe deer (*Odocoileus* ssp.). Provided by Håkan Strotz.	A.III
28	Meal of rye (*Secale cereale*). Carbonised at 200°C for two hours.	B.VII.c
29	Dried sap from birch (*Betula pendula*).	B.VII.c
30	Seeds of mustard (*Sinapis alba*). Carbonised at 200°C for two hours.	B.VII.a
31	Spruce (*Picea abies*) resin mixed with beeswax, 5:1, (Sandelin 1998)	C.X
32	Spruce (*Picea abies*) resin mixed with tallow from cow (Bos taurus), 5:1, (Sandelin 1998).	C.X
33	Spruce (*Picea abies*) resin, (Sandelin 1998).	C.X
34	Spruce (*Picea abies*) resin mixed with wood-ashes, 5:1, (Sandelin 1998).	C.X
35	Spruce (*Picea abies*) resin mixed with tallow from cow (Bos taurus) and charcoal, 5:1:1, (Sandelin 1998).	C.X
36	Spruce (*Picea abies*) resin mixed with tallow from cow (Bos taurus) and charcoal, 5:5:1, (Sandelin 1998).	C.IX
37	Carbonised hulled barley (*Hordeum vulgare*) from 17th century. Provided by Kerstin Griffin.	A.II
38	Carbonised hulled barley (*Hordeum vulgare*) from late 13th century. Provided by Kerstin Griffin.	B.IV
39	Carbonised naked barley (*Hordeum vulgare* var. *nudum*), c. 3700 BP. Provided by Kerstin Griffin.	B.VIII

Sample	Description	Cluster
40	Carbonised residues from birch-bark tar production.	A.I
41	Pine (*Pinus sylvestris*) resin mixed with tallow from cow (Bos taurus) and wood-ashes, 5:1:1, (Sandelin 1998).	C.X
42	Pine (*Pinus sylvestris*) pitch, moderately heated (Sandelin 1998).	C.X
43	Pine (*Pinus sylvestris*) resin mixed with beeswax, 5:1, (Sandelin 1998)	C.X
44	Pine (*Pinus sylvestris*) pitch, intensely heated (Sandelin 1998).	C.X
45	Pine (*Pinus sylvestris*) resin mixed with tallow from cow (Bos taurus) and charcoal, 5:5:1, (Sandelin 1998).	C.IX
46	Pine (*Pinus sylvestris*) resin (Sandelin 1998).	C.X
47	Pine (*Pinus sylvestris*) resin mixed with wood-ashes, 5:1, (Sandelin 1998).	C.X
48	Dried meat from baltic herring (*Clupea harengus harengus*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.b
49	Root from Lesser Celandine (*Ranunculus ficaria* ssp. *bulbilifer*). Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.c
50	Dried meat from grey seal (*Halichœrus grypus*). Carbonised at 300°C for two hours.	A.II
51	Dried meat from grey seal (*Halichœrus grypus*).Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.b
52	Thyme (*Thymus* sp.). Carbonised at 200°C for two hours.	B.VII.a
53	Funnel chanterelle (*Craterellus tubiformis*). Carbonised at 200°C for two hours.	B.VII.c
54	Dried meat from cod (*Gadus morhua*).Carbonised at 200°C for two hours.	B.VII.b
55	Dried meat from cod (*Gadus morhua*).Carbonised at 200°C for two hours. Treated with 12% hydrochloric acid for 30 minutes, rinsed with acetone and treated with hydrogen peroxide for 30 minutes.	B.VII.d
56	Iron Age food residue from northern Norway, with vegetables as the main component and possible traces of milk fat (Isaksson et al 1999).	B.IV
57	Iron Age food residue from northern Norway, with vegetables as the main component and a minor contribution of milk fat (Isaksson et al 1999).	B.IV
58	Iron Age food residue from northern Norway, with terrestrial mammal meat as the main component and a minor contribution of vegetables (Isaksson et al 1999).	B.V
59	Meal of wheat (*Triticum aestivum*). Carbonised at 300°C for two hours.	A.I
60	Root of wild carrot (*Daucus carota* ssp. *carota*). Carbonised at 200°C for two hours.	B.VII.c
61	Glue made from moose (*Alces alces*) skin. Produced by Håkan Strotz.	B.V
62	Glue made from moose (*Alces alces*) sinew. Produced by Håkan Strotz.	B.V
63	Glue made from moose (*Alces alces*) sinew, produced by Håkan Strotz, and mixed with birch-bark tar, 5:1.	B.VI
64	Fat extracted from moose (*Alces alces*) hoofs. Produced by Håkan Strotz.	A.III
65	Fat extracted from moose (*Alces alces*) bone-marrow. Produced by Håkan Strotz.	A.III
66	Fat extracted from moose (*Alces alces*) bone-marrow and hoofs. Produced by Håkan Strotz.	C.IX
67	Carbonised peas (*Pisum sativum*) from late 16th - early 17th century. Provided by Kerstin Griffin.	B.VII
68	Carbonised peas (*Pisum sativum*) from late 13th century. Provided by Kerstin Griffin.	B.IV
69	Early Iron Age organic residue from Öggestorp, Småland, with vegetables as the main component and a minor contribution of resin acids from Pinaceae and Betulaceae (Olander 1999).	B.VII.c
70	Pitch from birch-bark (*Betula pendula*).	