

C.Lemorini (LTFAPA, Sapienza University) S.Nunziante Cesaro (SMATCH)

Database of residues of plant and animal origin analyzed with the InfraRed technique on replicas made of stone or bone

Introduction to database

The database collects a selection of replicas made of stone or bone on which significant residues were observed and spectroscopically analyzed with the InfraRed technique.

This database was sponsored by the Wenner-Gren Foundation (NY) as part of a project aiming to verify the presence of micro-residues at the working edges of lithic archeological items by means of a non invasive method.

To identify the nature of the micro-remains, a set of suitable replicas which worked fleshy tissues, hide, bone, antler, shells and a large variety of domestic and wild vegetables was analysed.

This database is a work in progress. We will constantly add new spectra of replicas acquired during our research projects.

Replicas

Replicas of artefacts made of flint, obsidian, bone have been employed in a large series of activities such as butchering, working hide, hard animal material, cutting of wild and domestic cereals, reeds, grasses, edibles, medicinal, dyeing plants.

Experimental

FT-IR analysis of artifacts: Unused parts and working edges of archaeological and experimental chipped artefacts have been studied by means of Fourier Transform Infrared (FTIR) microspectroscopy using the Hyperion 2000 (Bruker Optics) microscope at the DA \square NE laboratories of the Istituto Nazionale di Fisica Nucleare, Frascati (Rome), Italy. Spectra were obtained cumulating at least 200 scans at a resolution of 2 cm⁻¹ or better. In the following, spectra of unused part of the tools are reported in black.

References

ANIMAL RESIDUES

T. Bereuter, C. Reiter, W. Mikenda, "Dead, drowned and dehydrated" Chemistry in Britain 35 (1999) 25-28

S. Gunasekaran, G. Ambalagan, S. Pnadi "Raman and Infrared spectra of carbonates of calcite structure" Journal of Raman Spectroscopy 37 (2006) 892-899

M. Jackson, Lin-P'ing Choo, P.H. Watson, W.C. Holliday and H.H. Mantsch "Beware of connective tissue proteins: assignment and implications of collagen absorptions in infrared spectra of human tissues" Biochim. Biophys. Acta 1270 (1995) 1-6

Y. Dauphin "Potential and Diffuse Reflectance Infrared Fourier Transform (DRIFT) Method in Paleolotological Studies of Bones" Applied Spectroscopy 43 (1993) 52-55

P. Dumas, L. Miller "Biological and Biomedical Application of Synchrotron Infrared Microspectroscopy" Journal of Biological Physics 29 (2003) 201-218

L. Bachmann, R. Diebolder, R. Hibst, D. M. Zezell "Infrared Absorption Bands of Enamel and Dentin Tissues from Human and Bovine Teeth" Applied Spectroscopy Review 38 (2003) 1-14

L. Köpper. H. M. Heise, F. G. Bechara, M. Stöcke. "Micro-domain analysis of skin samples of moor mummified corpses by evanescent wave infrared spectroscopy using silver halide fibers" Journal of Molecular Structure 565-566 (2001) 497-504

M. Cotte, P. Walter, G. Tsoucaris "Studying skin of an Egyptian mummy by infrared microscopy". Vibrational Spectroscopy 38 (2005) 159-167

D. Bikiaris, Sister Daniilia, S. Sotiropoulou, O. Katsimbiri, E. Pavlidou, A.P. Moutsatsou, Y. Chryssoulakis, "Ochre-differentiation through micro-Raman and micro-FTIR spectroscopies: application on wall paintings at Meteora and Mount Athos, Greece" Spectrochimica Acta Part A 56 (1999) 3–18

PLANT RESIDUES

M. Carbonaro, P. Maselli, P. Dore, A. Nucara "Application of Fourier transform infrared spectroscopy to legume seed flour analysis" Food Chemistry 108 (2008) 361-368

G. Giachi, B.Pizzo, N. Macchioni. I. Santoni "Caratterizzazione chimica del degrado di campioni di legno archeologico imbibito: confronto fra diverse metodologie di analisi" Gradus 3 (2008) 91-103

J. Kong, S. Yu "Fourier Transform Infrared Spectroscopic Analysis of protein Secondary Structures". Acta Byochimica and Byophysica Sinica 39 (2007) 549-559

M. Schwanninger, J.C. Rodrigues, H. Pereira, B. Hinterstoisser "Effects of short-time vibratory ball milling on the shape of FT-I spectra of wood and cellulose". Vibrational Spectroscopy 36(2004) 23-40

GENERAL REFERENCES

Lemorini C., Nunziante-Cesaro S. (eds) An Integration of the Use-Wear and Residue Analysis for the Identification of the Function of Archaeological Stone Tools, BAR International Series 2649 (2014), Archeopress, Oxford.

G.Monnier, E.Frahm, B.Luo, K.Missal Developing FTIR microspectroscopy for analysis of plant residues on stone tools, Journal of Archaeological Science (2017). Doi: 10.1016/j.jas.2016.12.004

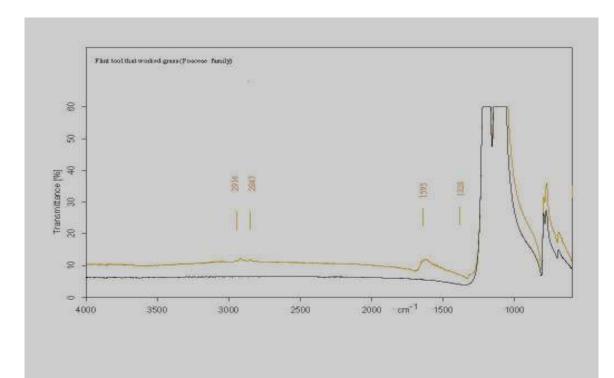
G.Monnier, E.Frahm, B.Luo, K.Missal Developing FTIR Microspectroscopy for the Analysis of Animal-Tissue Residues on Stone Tools, Journal of Archaeological Method and Theory (2018). Doi: 10.1007/s10816-017-9325-3

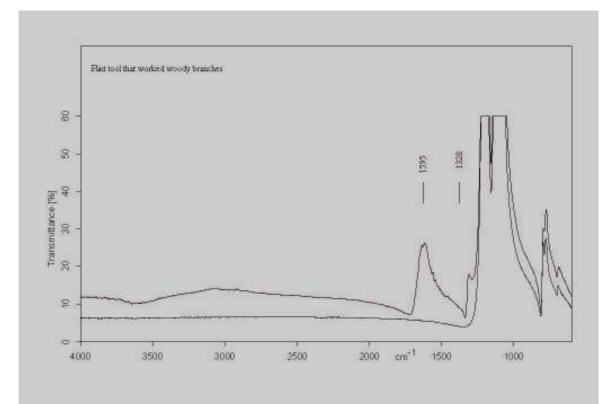
G.Monnier, K.May Documenting the degradation of animal-tissue residues on experimental stone tools : a multi-analytical approach, Archaeological and Anthropological Sciences (2019). Doi: 10.1007/s12520-019-00941-1

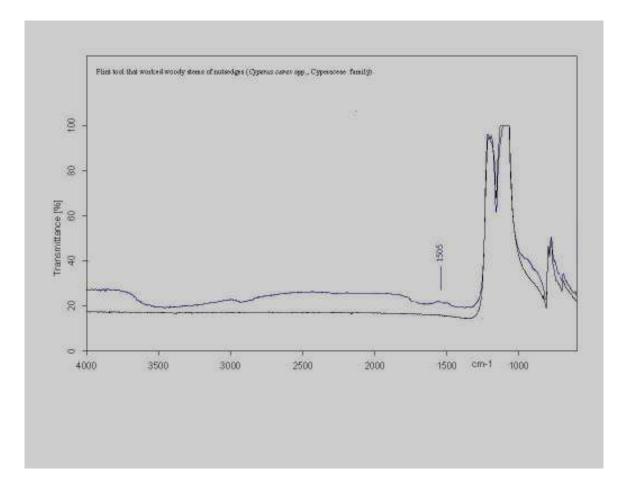
A.Nucara, S.Nunziante-Cesaro, F.Venditti, C.Lemorini A multivariate analysis for enhancing the interpretation of infrared spectra of plant residues on lithic artefacts, Journal of Archaeological Science: Reports (2020). Doi: 10.1016/j.jasrep.2020.102526

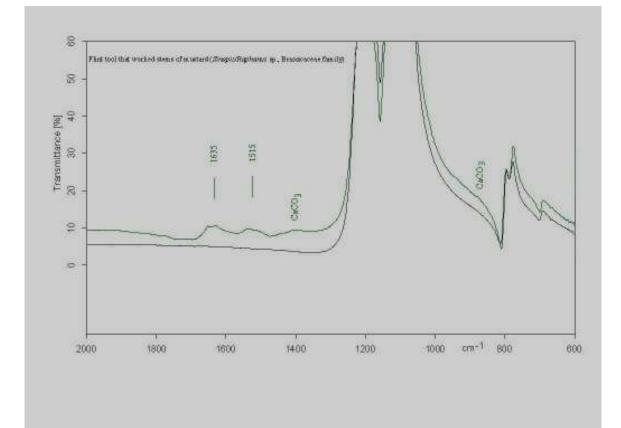
PLANT RESIDUES

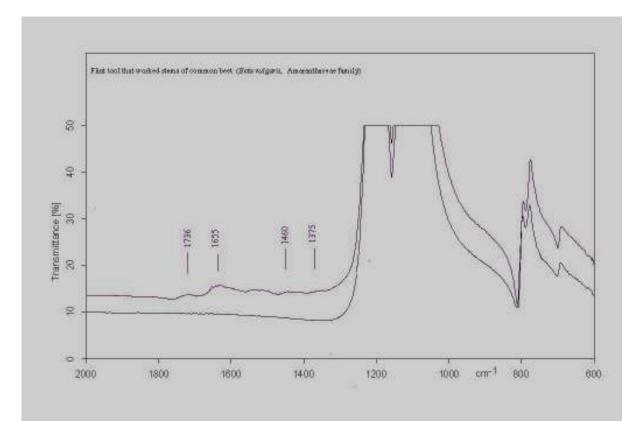
Wavenumber range (cm-1) of maxima	Proposed assignment
~ 3560	absorbed water weakly bound
3570 - 3450	valence vibration of H bonded O-H groups (intramolecular)
3400 - 3200	valence vibration of H bonded O-H groups
~ 3300	N-H stretching of proteins (Amide A)
~3100	N-H stretching of proteins (Amide B)
3000 - 2842	CH stretch in methyl and methylene groups
1730 – 1725	C=O valence vibration of acetyl or COOH groups
1738 – 1709	C=O stretch of unconjugated ketones, carbonyls and ester groups
~ 1700	C=O stretch of aldehydes or carboxylic acids
1690 – 1600	C=O stretching of proteins (Amide I)
1675 – 1655	C=O stretch of conjugated p-substituted aryl ketones
~1635	absorbed water
1605 – 1593	aromatic skeletal vibration
1515 - 1505	aromatic skeletal vibration
1576 - 1540	fatty acid salts carboxilate C-O stretching
1575 – 1480	C-N stretching + N-H bending of proteins (Amide II)
1470 - 1460	C-H deformation: asymmetric in -CH ₃ and -CH ₂
1430 – 1416	CH ₂ scissoring
1375 – 1374	CH deformation vibration
1370 - 1365	aliphatic CH stretch in CH ₃
1330-1325	phenolic OH
1301 – 1229	C-N stretching + N-H bending of proteins
1282 - 1277	CH deformation
1235 – 1225	OH plane deformation
1162 – 1125	C-O-C asymmetric valence vibration
1110 - 1107	Ring asymmetric valence vibration
~1086	C-O deformation in secondary alcohols and aliphatic ethers
1060 - 1015	C-O valence vibration
930 - 925	Pyran ring vibration
895 - 892	defomation. Ring valence vibration C-H- out of plane
858 - 853	C-H out of plane
767 – 625	O-C-N- bending of proteins (Amide IV)
800-640	N-H bending out of plane (Amide V)
606 - 537	C-O bending out of plane (Amide VI)

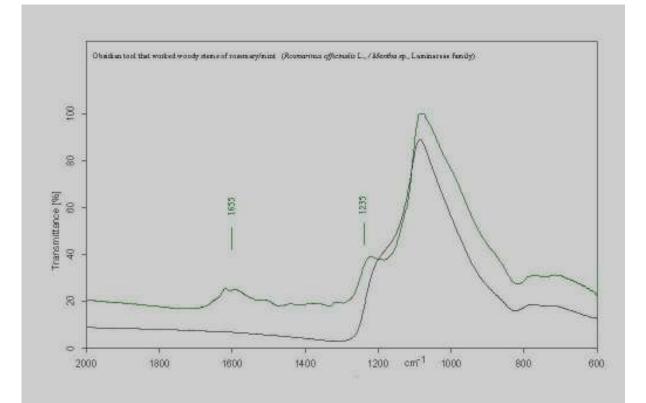


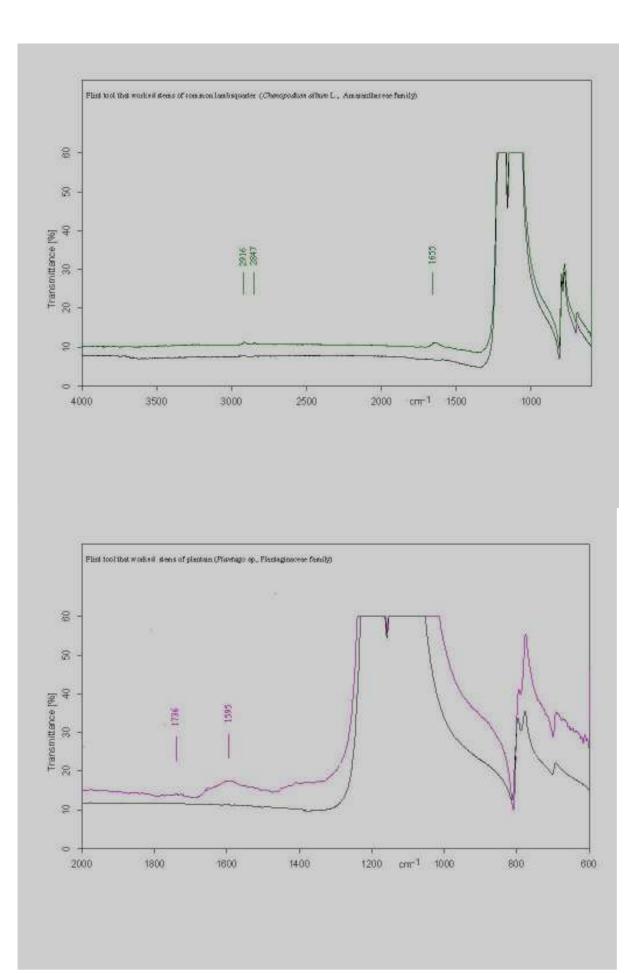


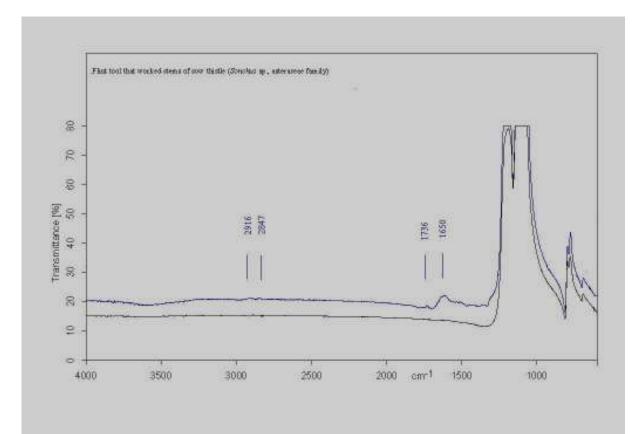


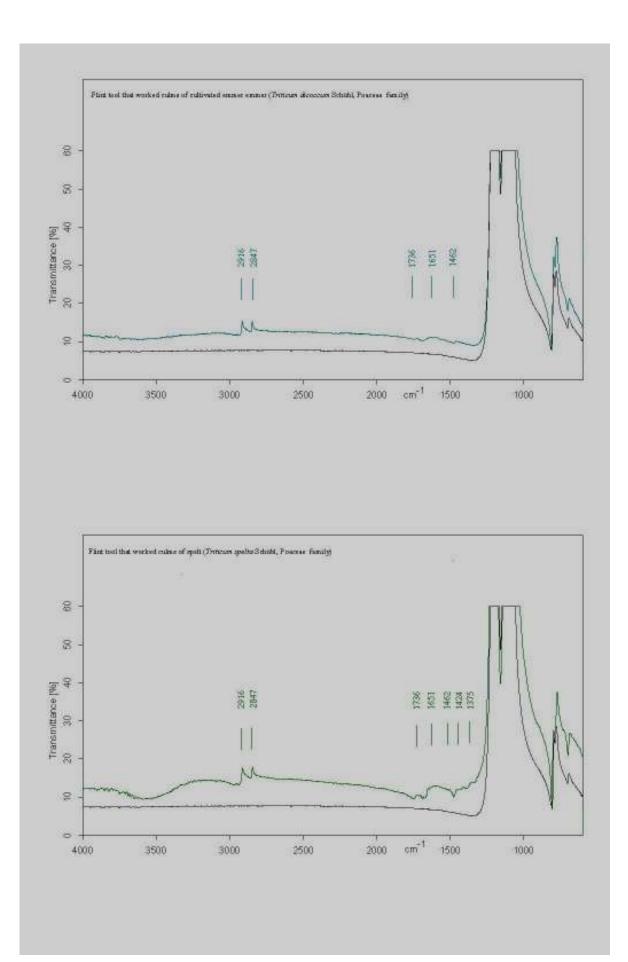


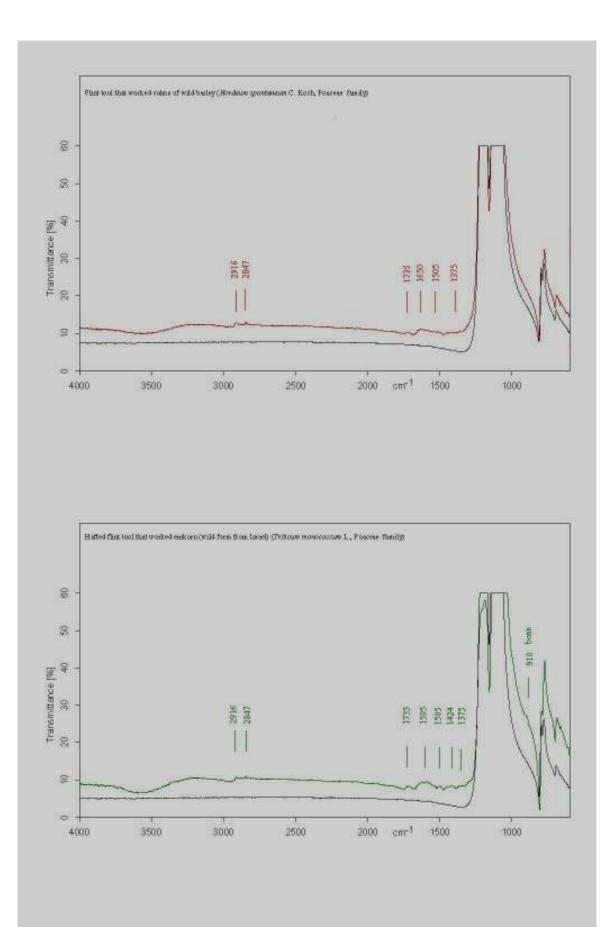


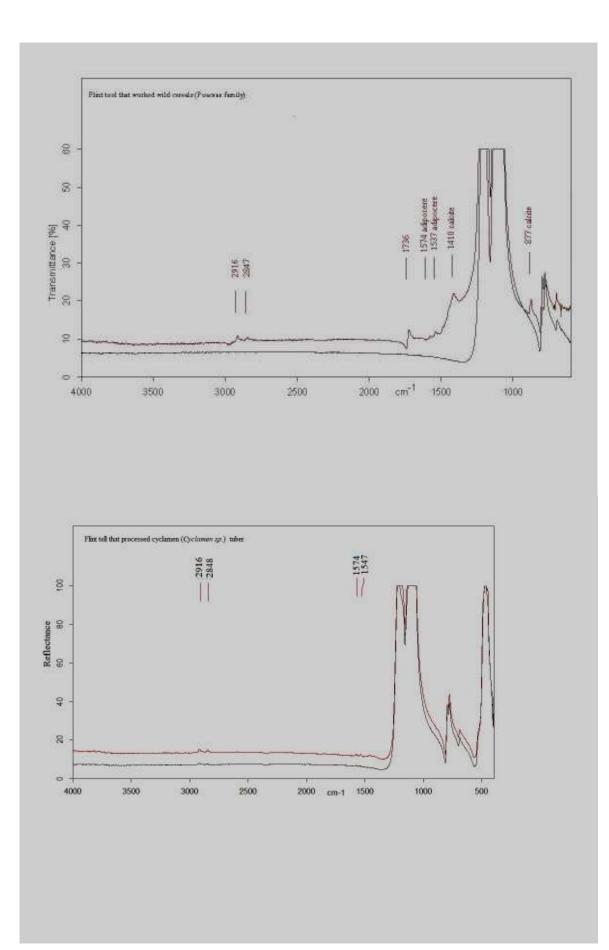


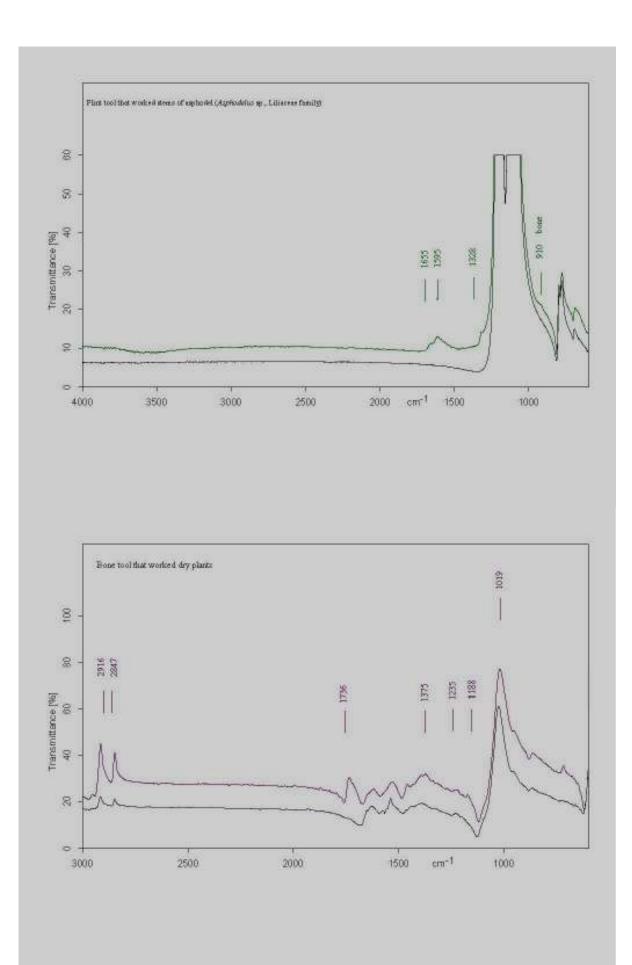


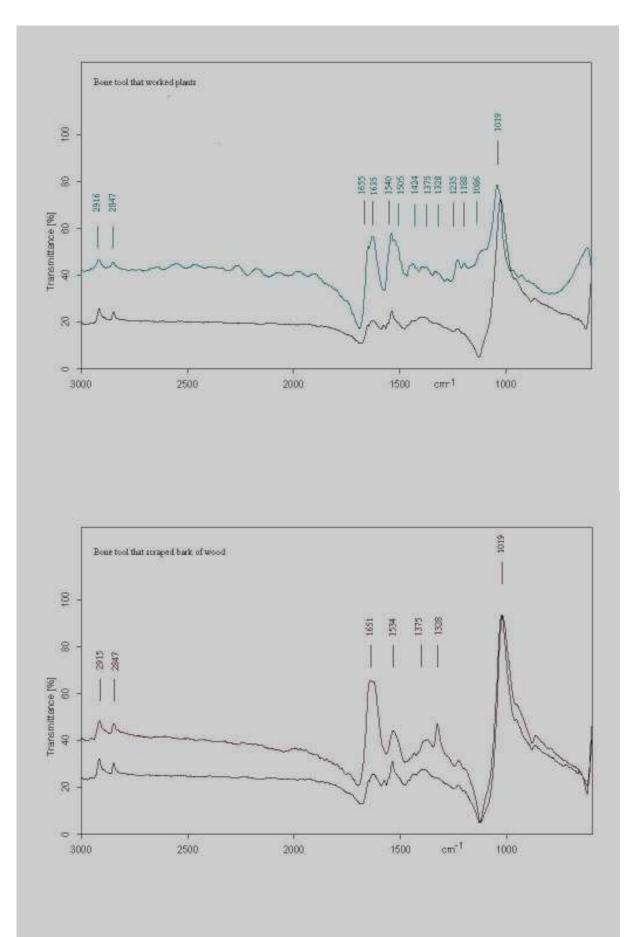


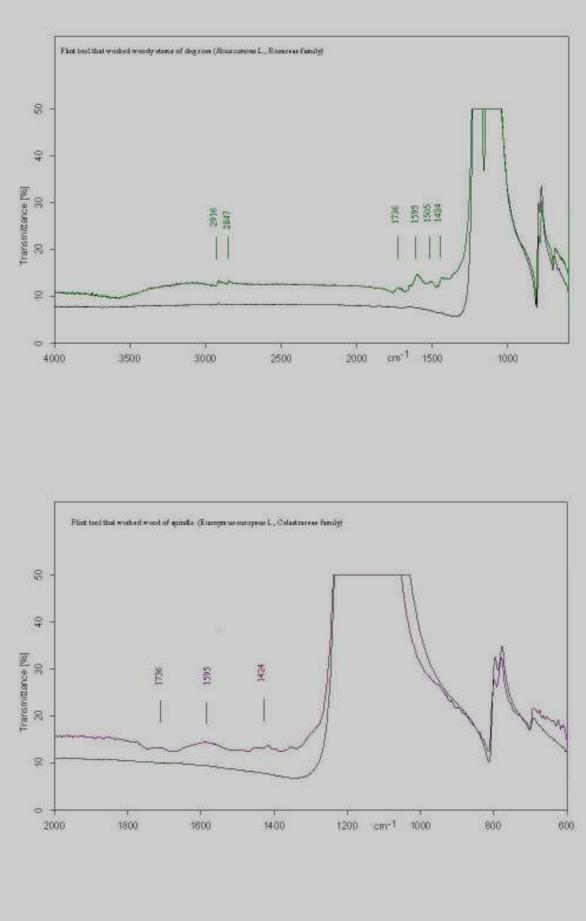


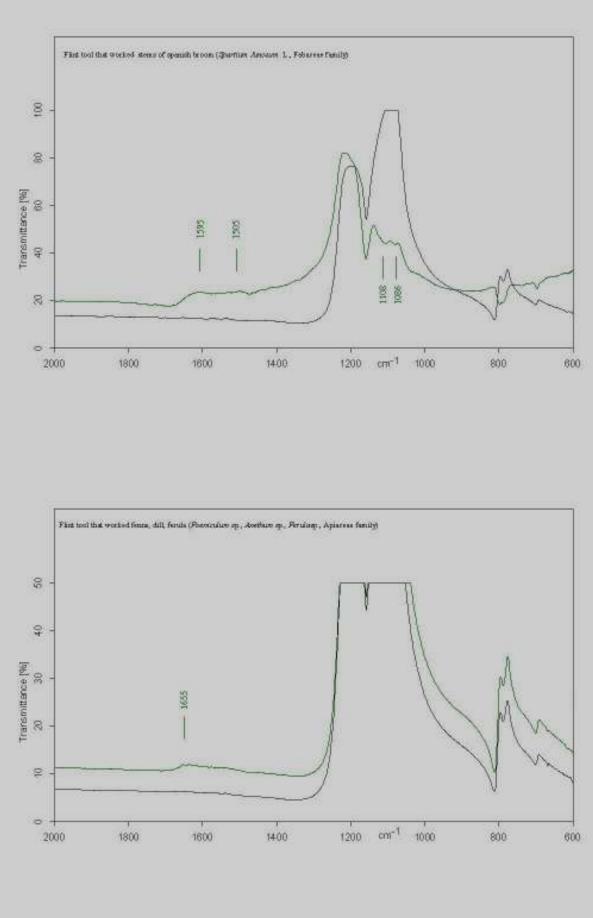


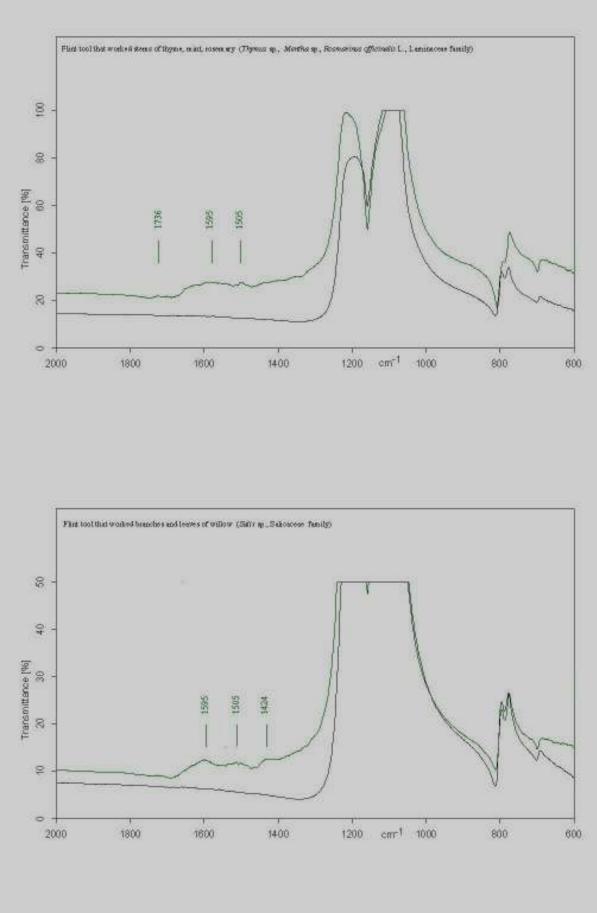


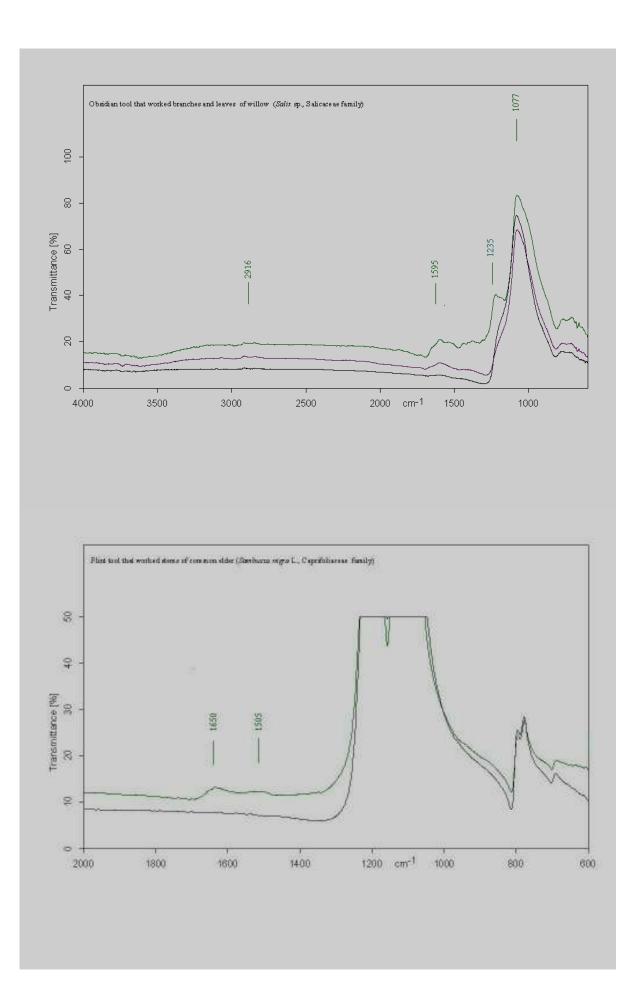


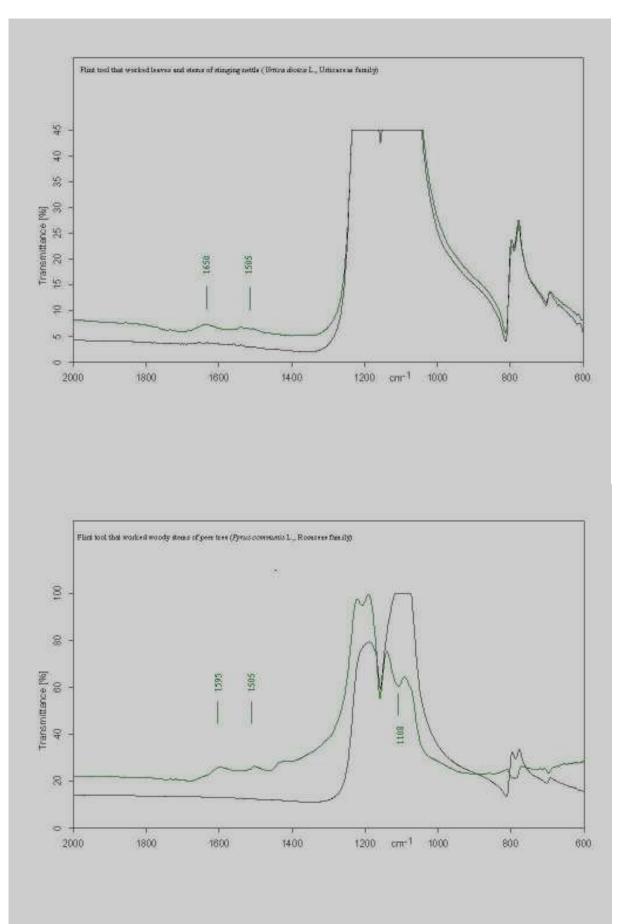


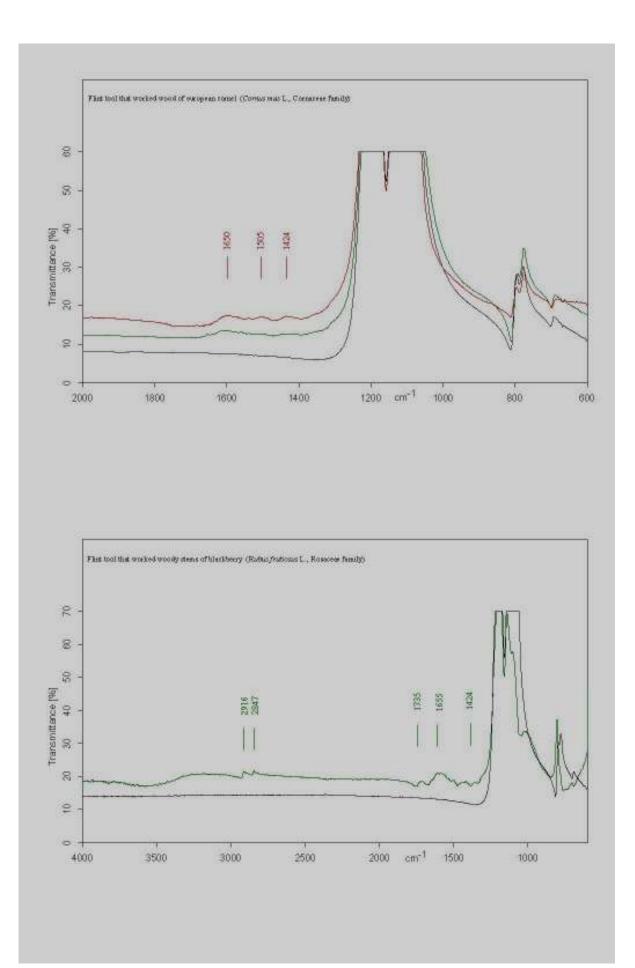


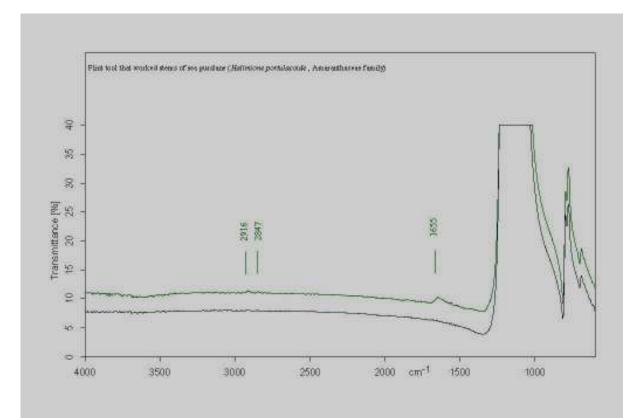












ANIMAL RESIDUES

Wavenumber range (cm-1) of maxima	Proposed assignment
~ 3560	absorbed water weakly bound
3570-3450	valence vibration of H bonded O-H groups (intramolecular)
3400 - 3200	valence vibration of H bonded O-H groups
~ 3300	N-H stretching of proteins (Amide A)
~3100	N-H stretching of proteins (Amide B)
3000 - 2842	CH stretch in methyl and methylene groups
~ 1735	C=O stretching of esters
1720 - 1710	C=O stretching of triacylglycerols
~ 1640	C=O stretching (amide I) of proteins
	fatty acid calcium salt carboxilate C-O stretching
1573	(adipocere)
~ 1540	NH + CN stretching of proteins (amide II)
1537	fatty acid calcium salt carboxilate C-O stretching (adipocere)
~ 1460	CH ₂ and CH ₃ deformation of proteins
1414	C=O stretching of calcite
~ 1030	Si-O stretching of kaolinite
~ 914	Si-O stretching of kaolinite
~ 910	PO ₄ ³⁻ stretching of apatite (bone)
877	CO ₃ ²⁻ stretching of calcite
~ 660	Al-Si-O bend of kaolinite

