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INVESTIGATION OF THE ADHESIVE RESIDUE ON THE FLINT INSERT AND THE ADHESIVE LUMP FOUND FROM THE PULLI EARLY MESOLITHIC SETTLEMENT SITE (ESTONIA) BY MICRO-ATR-FT-IR SPECTROSCOPY

The chemical composition of the flint insert and the black adhesive layer on it and of the adhesive lump found from the Early Mesolithic Pulli settlement site was determined by the attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectroscopy. The black adhesive lump and layer on the artefact is birch bark tar probably mixed with some fat and possibly containing some coniferous tree resin.

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Introduction

Combined tools made of organic and mineral materials were used across extensive regions in Eurasia during the Stone Age (e.g. Rimantene 1971, 164 ff.; Matyushin 1989, 130; Oshibkina 1997, 69; Vankina 1999, fig. XXIX). In functional sense we are mostly dealing with either arrow- or spearheads, in less frequent cases daggers or other tools. In the Baltic Sea region mostly combined tools were used during the Mesolithic, especially in its earlier phase. These tools were made by attaching inserts of flint (rarely quartz) to grooves carved into bone (or wooden?) points (e.g. Apals et al. 1974, plate 1; Jaanits et al. 1982, 30). Although such combined tools are rarely found, the inserts are discovered frequently. Adhesives were used to attach the inserts to the points, in few cases the remains of the adhesive have also been preserved. From some Stone Age sites in Scandinavia, Finland, Russia, Germany and Switzerland, adhesive lumps were found, sometimes with chewing marks (e.g. Vilkuna 1963; Apals et al. 1974 and references therein; Mikhail C. Zhilin pers. com. Aprill 22, 2009).

It is generally assumed that the adhesive was made of mixtures of (fir or pine) resin, birch bark tar, beeswax, fat, etc. (e.g. Jaanits et al. 1982, 30; Regert et al. 2003, 1622). In particular the use of birch bark tar has been emphasized, sometimes in combination with other materials (Stacey 2004, 1 and references therein). Nevertheless, there is no sufficient data available to make broad material usage generalizations across different areas of Europe. Therefore, the remains of adhesive found from Pulli, two cases of which will be discussed as follows, are definitely interesting for the wider public.

A flint insert with adhesive remains on it has been found from the Pulli Early Mesolithic settlement site (Fig. 1) in south-western Estonia, radiocarbon dated to 8700–8550 cal BC (Veski et al. 2005, table 2). This small (18 × 8 × 2 mm) microlith (AI 4476: 1042) is made of blackish brown flint blade knapped from creataceous flint. One of its edges is retouched and the end can be distinguished as a barb. There are remains of black adhesive on the surface of the artefact. From the same settlement site some small black lumps have also been found, which are probably pieces of adhesive. One of the lumps[1] (AI 4476: 662) is of irregular oval shape (49 × 16 × 13 mm, 5.2 g.) (Fig. 2) and has smooth surface.

The goal of the analyses was to determine the chemical composition of the flint insert and the black adhesive layer on it and of the adhesive lump, and also to determine whether the composition of the adhesive on the insert is similar to the lump. The samples were analysed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR FT-IR spectroscopy).

Infrared spectroscopy is an effective analytical method to study both organic and inorganic compounds. The vast majority of materials (e.g. oils, waxes, resins,

Fig. 1. The flint insert with adhesive remains (AI 4476: 1042).

[1] This has erroneously been taken for a schematic animal figurine of bone (e.g. Jaanits et al. 1982, 30; Kivimäe et al. 1998, 28).

Fig. 2. The adhesive lump (AI 4476: 662).

proteins, inorganic additives etc.) absorb infrared radiation and have rather characteristic infrared spectra (Regert et al. 2003; Vahur et al. 2005). Thus, classes of compounds can almost always be identified, in most cases even in mixtures. Identification of individual compounds in their pure forms is in many cases also possible. However, identification of individual compounds in mixtures is often difficult (depending on the complexity of the mixture).

There are various techniques of sample handling used in IR spectroscopy. The reflectance techniques such as ATR (Attenuated Total Reflectance) are increasingly used. ATR FT-IR spectroscopy is a non-destructive, fast and convenient method often requiring minimal sample preparation. With micro-ATR accessory it is possible to use very small sample size and the IR spectra can be measured directly from the sample surface. These are the reasons why micro-ATR sampling method was chosen for the present investigation.

Experimental

Samples

The following samples were analysed: the flint insert (Fig. 1), black adhesive layer on the flint insert and a lump (presumably adhesive, Fig. 2).

The main adhesives used in the prehistoric time were different wood tars (e.g. birch bark tar), different resins (e.g. pine resin) and their mixtures (Jaanits et al. 1982, 30; Regert et al. 2003, 1622). As stated above, these materials were probably used as adhesives for combined tools also in the Baltic region. In order to identify the adhesive materials, the spectra of birch bark tar and pine and fir resin (as the most probable ones in the Baltic geographic area) had to be registered. The pine (*Pinus sylvestris*) and fir (*Picea abies*) resin samples were of contemporary Estonian origin. The birch bark tar sample was prepared in Finland by methods of experimental archaeology carried out by Johanna Seppä.

The birch bark tar was obtained by thermal treatment of birch bark (*Betula alba*). The main constituents of birch bark are cellulose, tannins and oils. Birch bark tar has complex composition (Regert et al. 2006, 247 f.), containing different oils, phenolic compounds, sesquiterpenoids, partially decomposed cellulose, etc.

The samples did not need any special preparation. The spectrum of the insert was registered directly from the insert. Two pieces of the black thin adhesive layer were taken from the insert with a blunt scalpel and tweezers. The pieces of the black layer were easily removable. For the adhesive lump measurements, very small pieces of black sample were gently scraped from the adhesive lump. At first, the surface layer was scraped away and for the measurements of the IR spectrum, sample pieces from the inner part of the adhesive lump were scrabbled. Sample pieces were placed on the ATR crystal and force equivalent to 2.5 kg was used for pressing the sample pieces against the ATR crystal. After that the ATR-FT-IR spectrum was scanned.

Samples were taken from four different locations of the lump and all the IR spectra were very similar. The spectrum of the best quality is discussed in this paper.

Method

IR spectra were registered using a Nicolet 6700 FT-IR spectrometer equipped with the "Smart SplitPea" micro-ATR accessory. Thermo Electron's OMNIC Software was used for treatment of spectral data. The used FT-IR spectrometer has DLaTGS Detector, Vectra Aluminum Interferometer and sealed and desiccated optical bench with CsI optics.

The Smart SplitPea is a horizontal attenuated total reflectance (ATR) micro-sampling accessory for Thermo Electron's Nicolet FT-IR spectrometers. The SplitPea is designed for fast analysis of very small samples of bulk solids, powders and liquids using the ATR technique. The sampling area of the accessory has the diameter of 500 μm. The accessory has a diamond ATR crystal and calibrated pressure applicator with a 50x ViewThruPress. The following spectrometer parameters were used: resolution 4 cm^{-1}, spectral range 225–4000 cm^{-1}, number of scans: 128, Level of Zero filling: 0, Apodization: Happ-Genzel.

Results

IR spectrum of the flint insert

The IR spectrum of the flint insert is presented in Figure 3. In the IR spectrum it is possible to identify Si-O stretch vibrations characteristic of various forms of silica (SiO_2): at 1074 cm^{-1} there is the Si-O stretching band and the bending bands for Si-O occur at 797 cm^{-1}, 781 cm^{-1} and 462 cm^{-1} (Derrick et al. 1999, 114 ff.). Crystalline silica mineral quartz has an absorption band near 1100 cm^{-1} (the exact wave number depends on the type of silica), it also has a unique doublet band near 790 cm^{-1}, which is very characteristic (Derrick et al. 1999, 114 ff.) (Table 1).
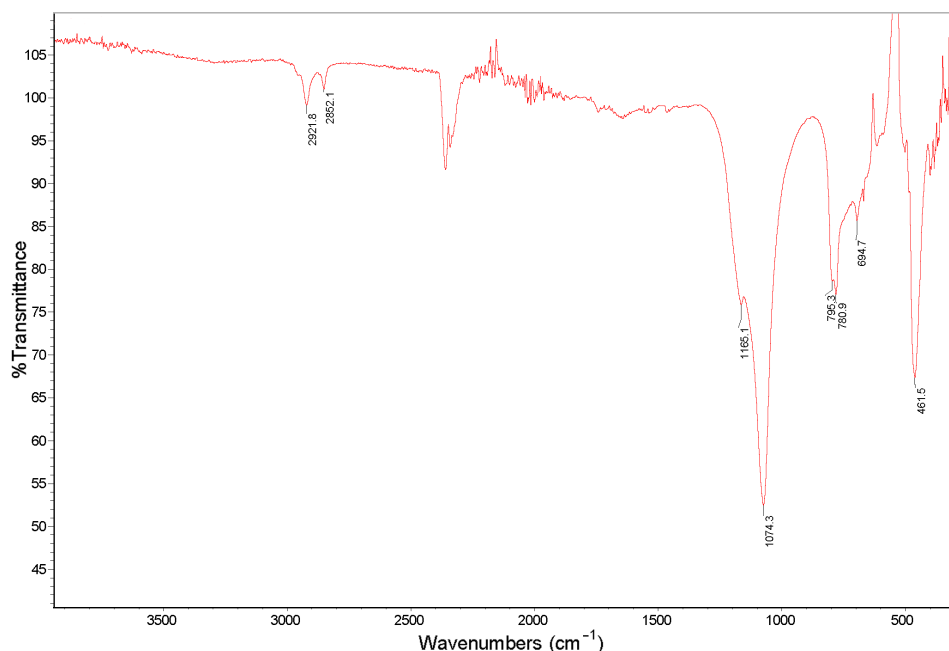
Fig. 3. IR spectrum of the flint insert.

Table 1. Bands wavenumbers in IR spectrum of flint insert

Band (cm^{-1})	Intensity	Assignment
2922, 2851	Weak	Aliphatic C-H stretch
1165, 1074	Strong	Si-O stretch
795, 781, 695, 462	Medium	Si-O bending

IR spectrum of the black adhesive layer on flint insert

Two spectra collected from different parts of the black adhesive layer on the flint insert are presented in Figure 4. A number of characteristic spectral features can be seen in the FTIR spectra of the black layer and these are presented in Table 2. The spectra are somewhat different but the main features are the same.

The spectral features can be rationalized as follows. A very broad OH stretch band appears in the region 3600–3000 cm^{-1}. OH groups are due to the phenolic compounds and alcohols and carboxylic acids formed via partial hydrolysis (and maybe oxidation) of the oils during the ageing. The intense C-H stretching vibrations appear at the region of 2919–2849 cm^{-1} and bending bands at 1456–1374 and 720–727 cm^{-1} (*cis*-C-H out-of-plane deformation). These bands are characteristic of alkyl fragments. In particular, the 720–727 cm^{-1} band is charac-
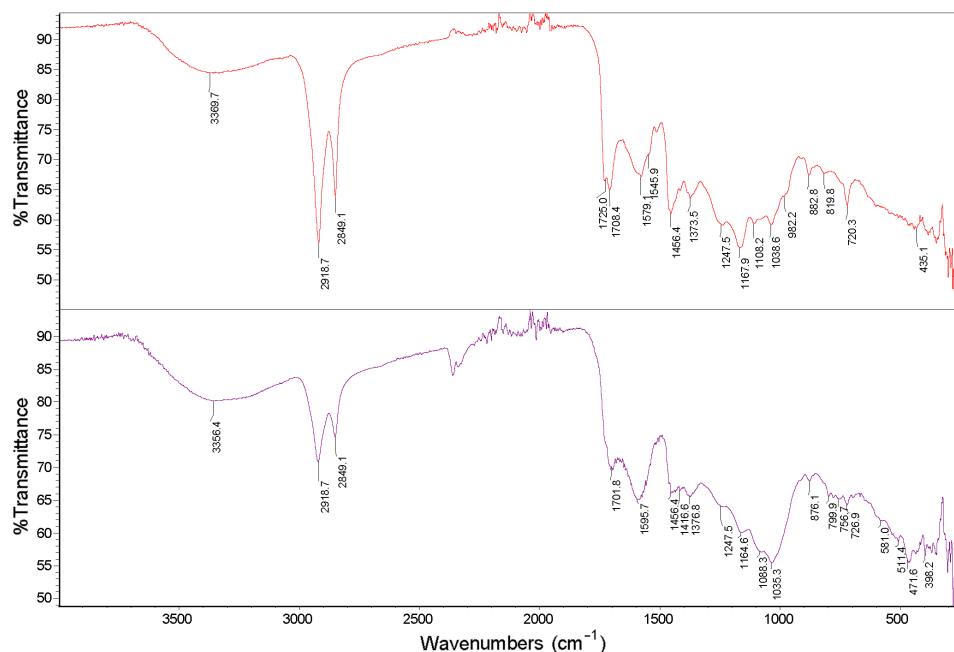
Fig. 4. IR spectrum of the black adhesive on flint insert.

Table 2. Bands wavenumbers in the IR spectra of black layer on insert

Band (cm^{-1})	Intensity, shape	Assignment (possible compound classes are given in brackets)
3600–3000	Medium, very broad	O-H stretch, hydrogen-bonded (alcohols, carboxylic acids, water)
2919–2849	Strong peak with two maxima	Aliphatic C-H stretch (alkyl groups)
1725–1700	Strong	C=O stretch (esters, ketones, aldehydes)
1600–1540	Medium, broad	Near ~1597 cm^{-1} aromatic ring (C-C) stretch; near ~1540 cm^{-1} asymmetric C-O stretch (carboxylates)
1456–1374	Medium	C-H deformation (alkyl groups)
1248	Weak	C-O stretch (esters, alcohols)
1168–1088	Medium	C-O-C stretch (esters)
1035–1039	Variable	C-O stretch or Si-O stretch (alcohols, silicates)
720–727	Weak	C-H wagging (alkyl groups)

teristic of compounds containing long aliphatic chains (typical in oils). Intense carbonyl (C=O) bands can be seen at around 1730 and 1700 cm^{-1}. Esters, ketones, aldehydes and carboxylic acids have C=O stretch bands in the region of 1750–1700 cm^{-1} (Meilunas et al. 1990, 38; Ahola 1993, 28 ff.). A carbonyl

in an ester occurs usually at 1750–1730 cm^{-1}, in a ketone usually at around 1720–1690 cm^{-1}, the carbonyl groups in aldehydes absorb in the range of 1740–1720 cm^{-1} (Derrick et al. 1999, 100 ff.) and carboxylic acids in the range of 1730–1700 cm^{-1} (Smith 1999, 245). Most likely the maxima at 1730 and 1700 cm^{-1} are mainly due to esters and carboxylic acids, respectively. The presence of esters also explains the C-O and C-O-C stretching bands appearing at 1260–1000 cm^{-1}. There is an interesting region in the range of 1600–1540 cm^{-1}. Skeletal vibrations from the C-C interactions in the ring absorb in the region 1600–1585 cm^{-1} and the asymmetric stretch of carboxylates appears at 1650–1540 cm^{-1} (Derrick et al. 1999, 100 ff.; Smith 1999, 245). Little evidence of the presence of significant amounts of aromatic compounds can be seen in the spectrum: there is very weak aromatic C-H stretch (3100–3000 cm^{-1}), and there are also no intense bands in the region of 700–800 cm^{-1}, which are very characteristic of aromatic compounds. This leads us to suggest that the broad band at 1650–1540 cm^{-1} is mostly due to carboxylate anions. The anions of the carboxylic acids were probably formed during long-time interaction of the material with the carbonaceous material in soil buffered at pH range above the pK_a values of carboxylic acids. There is a broad band between 1050 and 1000 cm^{-1}, which is present in one spectrum and absent in the other. This band is very characteristic of silicates and carbohydrates (incl. cellulose). In our case this may be due to either particles of sand or residues of plant material.

The appearance of the spectra suggests that the adhesive is a complex mixture containing different alkyl (and possibly aryl) compounds containing also hydroxyl and carbonyl groups.

IR spectrum of the adhesive lump

The spectrum of the sample piece of adhesive is presented in Figure 5. The spectrum matches exactly one of the arrowhead's black adhesive spectra.

IR spectrum of the reference birch bark tar

The reference spectrum of birch bark tar is presented in Figure 6. It is similar to the spectrum of the sample piece of adhesive (Fig. 5). Nevertheless, there are two distinct differences: the broad band in the region of 3600–3000 cm^{-1} and the band in the region of 1650–1540 cm^{-1} are very weak in the reference spectrum. As explained in the previous section, both these bands in the adhesive spectra may be due to carboxylic acids formed during decomposition of the original material on ageing. A more subtle, but possibly important difference, is the level of separation of the C-H stretch bands at ca 2920 and 2850 cm^{-1}. They are more clearly separated in the spectrum of the adhesive sample. This indicates higher content of compounds with long un-branched alkyl chains in the adhesive sample.
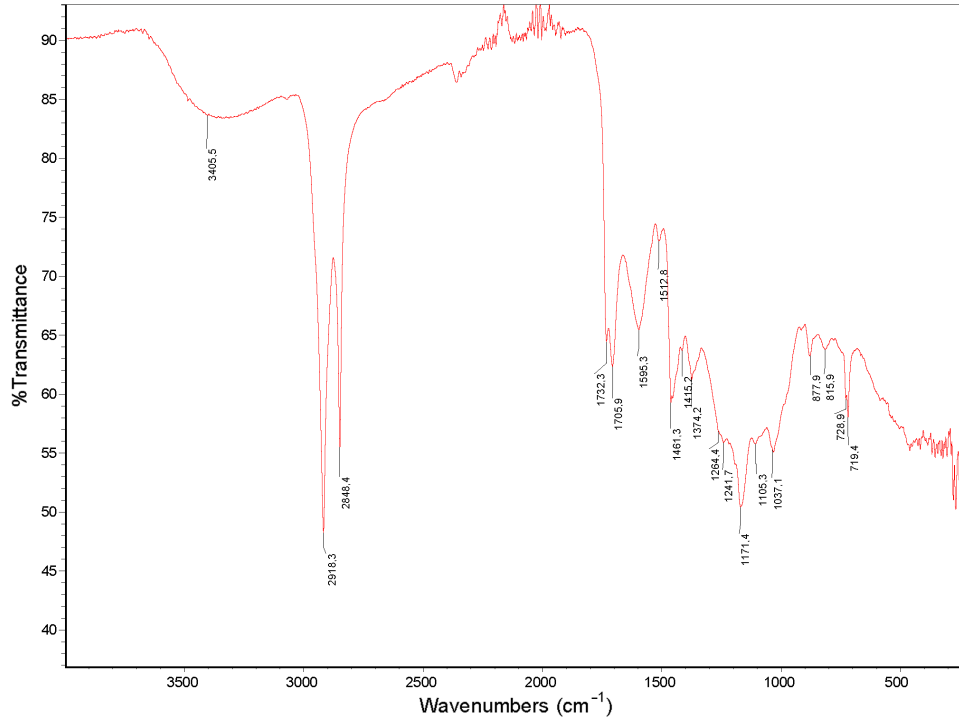
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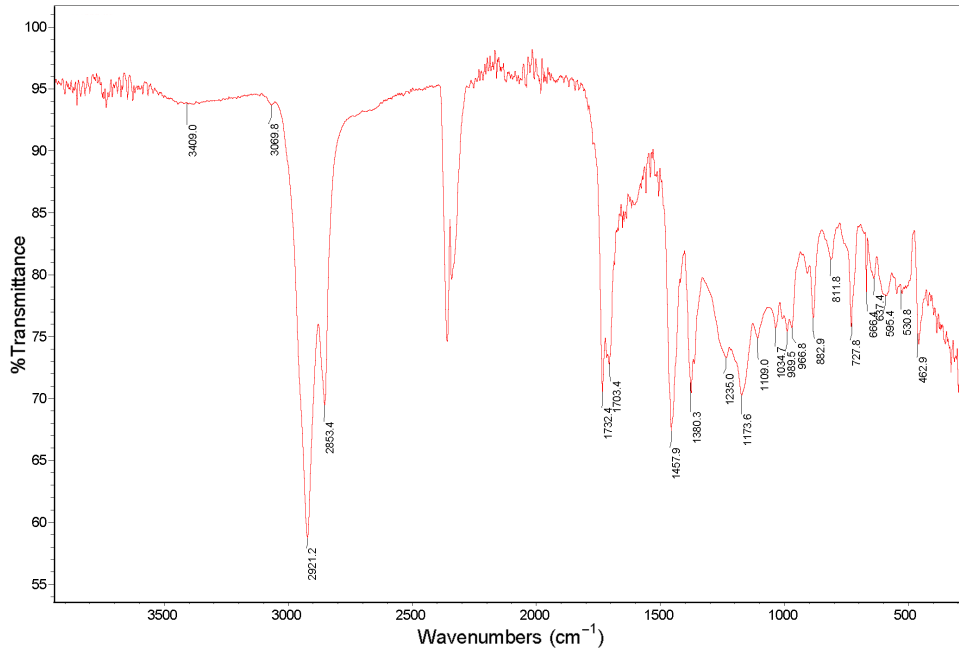**Fig. 5.** IR spectrum of the sample piece of adhesive.

Fig. 6. IR spectrum of the reference birch bark tar.

IR spectrum of the fir and pine resin

For reference, fir and pine resin spectra are presented in Figures 7 and 8. The spectra differ somewhat from each other and the following features distinguish them from the arrowhead's adhesive spectrum:

1. The two bands of the aliphatic C-H stretch group (with maxima between 2840 and 2930 cm^{-1}) are significantly less separated in resin spectra. This shape of the C-H stretch group is characteristic of highly branched and cycle-containing alkyl groups. Such alkyl fragments are common to terpenoid compounds that are the main constituent of fir and pine resins. In contrast to this, long straight alkyl chains display well separated maxima.

2. All resin spectra contain a very strong absorption at 1690 cm^{-1} (due to the carboxylic groups of resin acids), which is missing in the adhesive spectra. At the same time the adhesive samples have a prominent band at 1700–1720 cm^{-1} (due to esters), which is missing in the resin spectra.

3. The large group of bands centered around 1100–1000 cm^{-1}, which is a prominent feature in the adhesive spectra, is missing in the resin spectra.

In contrast to the adhesives, the resins used for recording the spectra are not of ancient origin. We therefore need to consider possible changes that could have
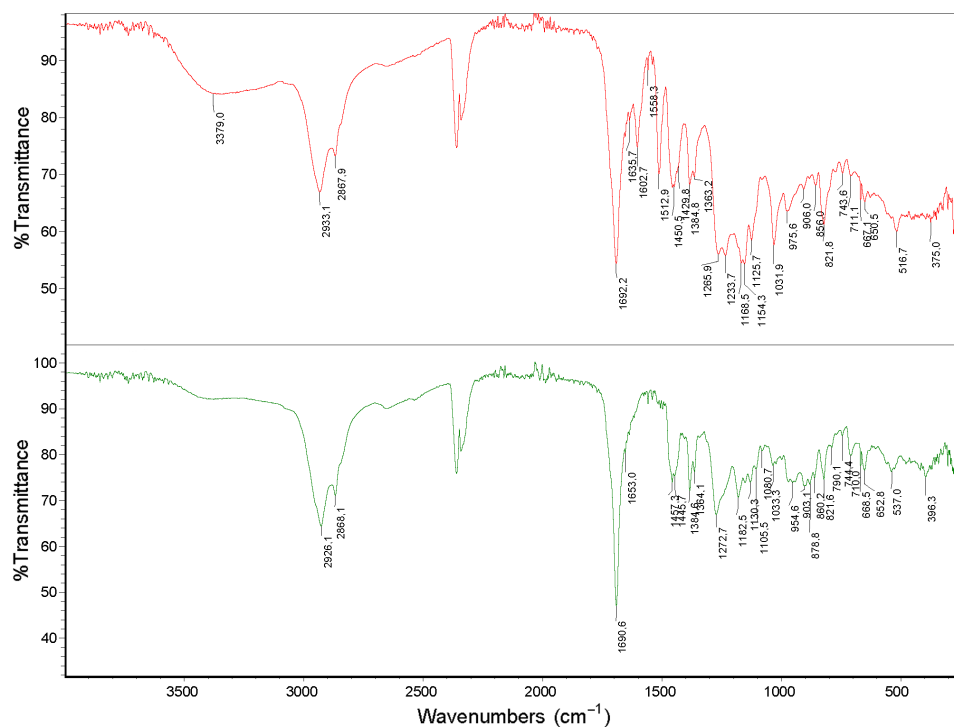

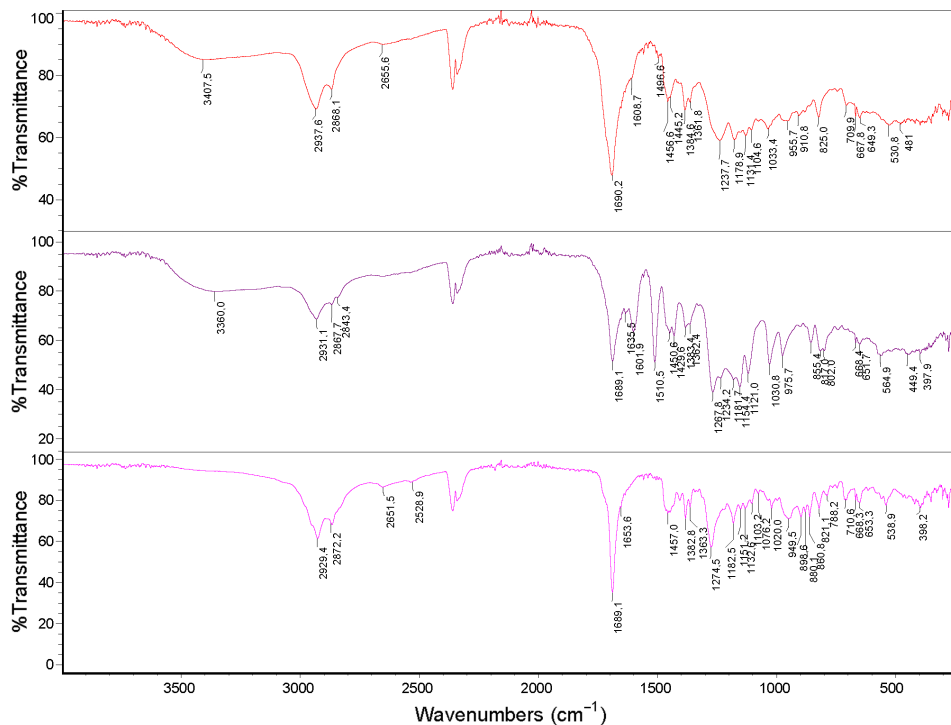
Fig. 7. IR spectra of fir resin.

Fig. 8. IR spectra of pine resin.

taken place during ageing. First of all these are related to the group of bands centered around 1100–1000 cm^{-1}, which are due to C-O and C-O-C stretch vibrations. These bands could emerge also in resin spectra upon oxidation of the resins. However, the two maxima of the aliphatic C-H stretch group cannot become more separated with time, which would be necessary for the adhesive to be a resin.

Discussion and conclusions

The ATR-FTIR spectroscopic analyses show that the spectrum of the adhesive lump exactly matches one of the insert's black adhesive spectra. Both adhesive spectra contain bands due to alkyl groups at 2918–2849 cm^{-1} (aliphatic C-H stretch) and 1461–1374 cm^{-1} (C-H deformation), carbonyl groups at 1732–1703 cm^{-1} (C=O stretch) and C-O stretches (and also C-O-C stretches) at 1264–1037 cm^{-1}.

The adhesive spectra differed considerably from the tree resin spectra, although the presence of some tree resin in the adhesive cannot be ruled out. At the same time the adhesive spectra correlated rather well with the birch bark tar spectrum. Comparing the IR spectrum of the birch bark tar to the adhesive spectra there are

three differences. (1) The broad band in the region of 3600–3000 cm^{-1} and (2) the band in the region of 1650–1540 cm^{-1} are very weak in the reference spectrum and (3) the C-H stretch bands at 2920 and 2850 cm^{-1} are better separated in the spectrum of the adhesive sample.

The broad bands 3600–3000 cm^{-1} and 1650–1540 cm^{-1} in the adhesive spectra may be due to carboxylic acids formed during decomposition of the original material on ageing. The better separation of the bands at 2920 and 2850 cm^{-1} indicates higher content of compounds with long un-branched alkyl chains in the adhesive sample. The most obvious material with long alkyl chains (and also ester groups contributing to the bands of C=O and C-O-C) is fat.

We can thus conclude that the black adhesive lump and layer in the flint insert is birch bark tar, probably mixed with some fat and possibly containing some pine or fir resin. If adhesive was made in what is now Estonia, resin can be only from pine, because in Early Mesolithic period fir did not grow in this area (e.g. Poska 2001, 13).

There are several more or less distant analogues to the results of the analyses from Pulli. While ethnographic parallels were previously used to interpret the finds of adhesives, then predominantly since the 1990s analytical methods have been applied to study various amorphous substances (Regert et al. 2003, 1620 and the references therein).

Because organic material is poorly preserved in soil, this kind of finds, especially in case of the Stone Age, are rare. We are usually dealing with bone or antler, more seldom wooden, artefacts. Only in exceptional cases organic substance can be found, and in these cases it is possible to speculate that it might have been used as an adhesive. However, this kind of unique substances have been documented on European prehistoric artefacts already for more than hundred years (e.g. Regert et al. 2003, 1621 and the references therein). In our neighbouring countries more attention to the topic has been paid in Finland and in Scandinavia, where lumps of organic substance have been found from several settlement sites. While bite marks can often be observed on these pieces, the bits have also been interpreted as chewing resin (e.g. Pälsi 1932; Kopisto 1963; Vilkuna 1963; Edgren 1984, 761). Middle and Late Neolithic pottery sherds repaired with adhesive have also been found in Finland. The adhesive has been identified as birch bark tar (Pesonen 1994; 1999 and references therein; Reunanen & Holmbom 1999). Birch bark tar is identified also in a number of Iron Age artefacts in Europe (e.g. Stacey 2004 and the references therein).

In Estonia organic adhesive on bone artefacts has been already described in the 19th century (Grewingk 1882, plate III). More recently organic adhesive has been observed on pottery sherds. However, the analyses of the pieces of the adhesive are unique in Estonia. Because no analyses of adhesives used to attach flint inserts have been conducted in our neighbouring areas, then the results we have gained are very difficult to place into a broader context. Whereas birch bark tar was a very common component in adhesives used for several purposes already from the Middle Paleolithic (Koller et al. 2001, 329) and was used even

later (e.g. Nykänen & Seppä 1997, 25; Stacey 2004), it can be assumed that it was one of the main adhesives used to complete combined artefacts during the Stone Age in Europe.

Acknowledgements

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PULLI ASULAKOHAST LEITUD TULEKIVIST PISTIKTERA KITI JA KITIKAMAKA UURINGUD MIKRO-ATR-FT-IR-SPEKTROSKOOPIA MEETODIL

Resümee

Orgaanilisest ja mineraalsest materjalist kombineeritud tööriistu valmistati kivi-ajal Euraasias laiadel aladel. Funktsionaalselt on enamasti tegemist kas noole- või odaotste, harvem pistodade või teiste esemetega. Läänemere piirkonnas kasutati kombineeritud tööriistu peamiselt mesoliitikumis, eriti selle varasel perioodil. Tööriistad valmistati tulekivist (harvemini kvartsist) pistikterade lisamisega luust (või puust) teravike servadesse tehtud uuretesse. Mõningatel juhtudel on säilinud ka pistikterade kinnitamiseks kasutatud kitti.

Varamesoliitiliselt Pulli asulakohalt Edela-Eestis on leitud üks tulekivist pistik-tera, millel on näha musta massi – oletatavasti kitijäänuseid (joon 1). Asula kultuur-kihist on leitud ka väikesi musta või mustjaspruuni värvi kamakaid, mis visuaalselt on sarnased eelkirjeldatud pistiktera pinnal oleva massiga. Mikro-ATR-FT-IR-spektroskoopia meetodil uuriti nii pistiktera ja selle pinnal olevat ainet kui ka üht suuremat oletatavat kitikamakat (joon 2). Kuna on põhjust oletada, et esiajaloo-lisel ajal kasutati kittainetena peamiselt erinevate puude tõrva ja vaiku või nende segusid, siis analüüsiti võrdluseks ka Eestist pärit männi- ning kuusevaiku ja Soomes Johanna Seppä eksperimentaalselt valmistatud kasetõrva.

Infrapunaspektrid (IR-spektrid) registreeriti, kasutades teemantkristalliga ATR-(ehk nõrgendatud täieliku sisepeegeldusega) mikroanalüsaatorit (Smart SplitPea), mis on paigaldatud Nicolet 6700 FT-IR-spektromeetrile. Spektromeetrit juhiti ja spektreid töödeldi programmis Thermo Electron's OMNIC. Smart SplitPea on horisontaalne ühepõrkeline mikro-ATR-seade, mis võimaldab analüüsida väga väikesi tahkeid proovikoguseid, pulbreid ja vedelikke. IR-spektrite registreerimiseks kasutati järgmisi spektromeetri parameetreid: lahutusvõime 4 cm^{-1}, mõõtepiirkond 225–4000 cm^{-1}, keskmistatavate spektrite arv 128 ja apodisatsioon Happ-Genzel.

Tulekivist pistiktera IR-spektri (joon 3, tab 1) põhjal on võimalik identifitseerida Si-O neeldumisjooni, mis on iseloomulikud erineva kujuga ränioksiididele (näiteks mineraalne kvarts, mis on kristalliline ränioksiid).

IR-spektrite registreerimiseks võeti tulekivist pistikteralt kahest erinevast kohast musta kittainet. Need kaks spektrit erinevad veidi teineteisest (joon 4, tab 2), samas on aga põhilised tunnusjooned mõlemal samad. IR-spektritest selgub, et must mass on keerulise koostisega segu. IR-spektrites esinevad alküülrühma, hüdroksüülrühma (kuulub alkoholidele ja karboksüülhapetele), karbonüülrühma (kuulub arvatavasti estritele ning karboksüülhapetele) ja C-O-C (kuulub estritele) neeldumisjooned. Lisaks esinevad spektrites veel aromaatsetele ühenditele ja silikaatidele (liiva üks koostiskomponent) või süsivesikutele (tekkinud taimede jääkidest) kuuluvad neeldumisjooned.

Oletatava kitikamaka spekter (joon 5) on sarnane pistiktera pinnal oleva musta aine spektriga.

Võrdluseks analüüsitud kasetõrva IR-spekter (joon 6) on üsna sarnane kitikamaka IR-spektriga (joon 5). Sellest hoolimata on olemas paar selget erinevust: võrdlusspektris lai neeldumismaksimum piirkonnas 3600–3000 cm^{-1} ja neeldumine piirkonnas 1650–1540 cm^{-1} on väga madala intensiivsusega. Lisaks on lainearvude vahemikus 2920–2850 cm^{-1} olevate C-H neeldumisjoonte kujus võimalik erinevusi näha.

Kuuse- ja männivaigu IR-spektrid (joon 7 ja 8) erinevad mõnevõrra teineteisest. Kui võrrelda kuuse- ja männivaigu IR-spektreid pistiktera pinnal oleva musta liimaine spektriga, on erinevused C-H valentsvõnkumiste (2840–2930 cm^{-1}), karbonüülrühma (vaikudel on neeldumine 1690 cm^{-1} juures) ja 1100–1000 cm^{-1} piirkonnas. Erinevalt pistiktera pinnal olevast kitist ei ole vaigud pärit esiajaloolisest ajast. Seega tuleb kiti seisukohalt arvestada muutustega, mis on toimunud vananemise tagajärjel (IR-spektris on näha põhilisi muutusi vahemikus 1100–1000 cm^{-1}, kus asuvad C-O ja C-O-C valentsvõnkumised).

Kokkuvõttes nähtub, et kitikamaka ja pistiktera pinnal oleva musta aine ATR-FT-IR-spektrid on väga sarnased. Mõlema kiti IR-spektrid sisaldavad alküülrühma (C-H), karbonüülrühma (C=O) ja C-O ning C-O-C võnkumiste neeldumismaksimume. Musta aine IR-spektrid erinevad märgatavalt männi- ja kuusevaigu IR-spektritest, samas ei saa välistada mõne puuvaigu lisandi olemasolu kitis.

Musta kiti IR-spektrid sarnanevad märgatavalt kasetõrva IR-spektriga. Samas on spektrites näha mõningaid erinevusi. Kiti spektris esinevad neeldumisjooned

lainearvude piirkonnas 3600–3000 cm^{-1} ja 1650–1540 cm^{-1} karboksüülhappe lisandi tõttu, mis on tekkinud tõenäoliselt originaalmaterjali vananemise taga-järjel (need neeldumised on kasetõrva võrdlusspektris väga väikese intensiivsusega). C-H valentsvõnkumiste jooned lainearvude vahemikus 2920–2850 cm^{-1} on kiti IR-spektris paremini lahutunud kui kasetõrva omas. See erinevus näitab, et kase-tõrvaga võrreldes sisaldub kitis mõnevõrra rohkem pika alküülahelaga ühendeid. Rasv on selline materjal, mis sisaldab pika ahelaga alküülrühmi ja lisaks veel estreid.

Saadud tulemuste põhjal võib järeldada, et nii kitikamakas kui ka kitijäänused tulekivist pistikteral koosnevad suure tõenäosusega põhiliselt kasetõrvast, mille hulka on arvatavasti segatud rasva ja ehk ka okaspuuvaiku. Kui kitt on valmis-tatud Eesti alal, võib kõne alla tulla vaid mänd, sest kuusk toona siin veel ei kasvanud.