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# Fourier Transform Infrared Spectroscopy – Useful Analytical Tool for Non-Destructive Analysis

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## 1. Introduction

It is highly recognized that the use of Fourier Transform Infrared Spectrometry (FTIR) for chemical substances identification it is not a trivial task to be fulfilled by analytical chemists. The complexity of FTIR characterization comes mainly from the high degree of infrared absorption bands overlapping, that are difficult to be accurately ascribed, despite of the fact that up to date computer-searchable databases of spectra are currently available.

Regardless all these difficulties, FTIR analysis became the main used technique when specific analytical topics have to be addressed, mainly when non-destructive analysis is needed. In this respect, according to our opinion, challenging analytical issues are raised in two important cases; the first one is that when historic (archaeological) or artistic materials have to be analyzed while the second issue came from the analysis of highly- specific biomaterials. Starting from these points, the present chapter is addressing, as case studies, both issues: the FTIR assessment of peculiar archaeological samples, amber samples, and, respectively the FTIR assessment of a developed bio-mimetic system based on human lipoproteins immobilization on conductive solid supports. In both cases the restricted amount of samples and the emergent call for non-destructive analyses create constraints in the working procedure.

Consequently, we consider that the versatility of FTIR techniques (especially variable angle reflectance- FTIR, VAR-FTIR and attenuated transmittance-FTIR, ATR-FTIR) in solving these critical issues are presented and, moreover, supported with original experimental data.

## 2. Applicability of Fourier Transform Infrared technique in the assessment of archeological samples. Case study- Amber

Archaeology is a science dealing mainly with the reconstruction of past events by the mean of a cautious credentials and artefacts collection. Historical archaeologists usually encounter

on a list of so-called potential trace evidence, different items which require certain identification; the mentioned list may be formed by objects from various materials: paint, pottery, glass, bricks, liquid residues (oils, wines, and perfumes), fabrics, soil, metals etc. In order to rationalize on the evidences origin, source, transformation and historical age, the archaeologists need a deep analytical study, study that often has to be performed on irreplaceable pieces. Consequently, to accomplish these goals multiple analytical techniques, able to work as non-destructive techniques are used, such as: Fourier Transform Infrared Spectrometry (FTIR), scanning electron microscopy (SEM), polarized light microscopy (PLM) or X-photon spectrometry (XPS).

In our studies, in the amber analysis the main goal was to establish several criteria able to be useful in discrimination between different types of amber, the obtained FTIR information being used to ascribe the origin of the materials found in archaeological sites on the Romanian territory.

Amber is a fossil resin, extremely appreciated for its colour and beauty, and used as a gemstone from very early times. Natural amber deposits are found all around the world, the most famous being the ones from the Baltic sea, the Dominican republic, Sicily, Borneo, Spain, etc. Amber resources are documented in Romania since the late sixteenth century, around the village of Colți (Buzău County), but they have certainly been exploited only starting with the modern age, after 1828, in the same area (Ghiurcă, 1999; Wollmann, 1996).

The existence of a local amber exploitation on Romanian territory aroused the question of geological origin of amber artefacts found by Romanian archaeologists over time.

During recent years, analysts used mostly FTIR, mass spectrometry and pyrolysis-gas chromatography-mass spectrometry for the analytical study of geological or archaeological amber from different territories (Beck, 1972; 1986; Boon et al., 1993; Lambert & Poinar, 2002; Shadrinski et al., 2004; Angelini & Bellintani, 2005; Guiliano et al., 2007; Pakutinskiene et al., 2007; Tonidandel et al., 2008; Teodor ED et al., 2009; Vîrgolici et al., 2010a). In 2005, Angelini and Bellintani reviewed the analytical techniques used for the differentiation of amber types, dedicating special attention to the most suitable methods for archaeological materials (non-destructive methods).

There are a few comparative analytical studies of Romanian geological amber, referred to as Rumanite or Romanite, which conclude that Romanian amber is geologically younger, but chemically almost identical, to Baltic amber (Stout et al., 2000).

Regarding archaeological amber from Romanian territory, it was basically unstudied since we started our research project in 2007. Some studies by Nikolaus Boroffka on prehistoric amber (Boroffka, 2006) refer to chemical analyses of amber with an assumed Romanian origin; in another paper, Boroffka (2001) discusses the results published by Banerjee (Banerjee et al. 1999) for two prehistoric beads from Romania, both considered of Baltic origin.

As a hint for the archaeological output, in order to rationalize on the importance of non-destructive analysis, it should be mentioned that the quantity and quality of amber artefacts from Romania is lower than those found in territories placed on the track of the so-called Amber Route (Teodor ES et al, 2010). Nevertheless, from our studies, the Baltic amber is encountered very early, in Neolithic, i.e. only three isolated beads (not published), and only in southern Romania, as a clue that Danube may be considered as a secondary Amber Trail.

Local amber, Romanite, was also early used, as proved on some beads from the Middle Bronze Age from Pietroasa Mică, in a necropolis placed at the fringes of the Colți area. In our studies two types of amber have been investigated: artefacts from the largest amber deposit discovered in Romania, in Cioclovina cave (over 3000 beads, most of them in amber) (Teodor ES et al., 2010) and artefacts from Roman Age; discovered in cemeteries dug systematically, for instance in Tomis, Callatis, Beroe, or Carsium cemeteries (Vîrgolici et al. 2010b).

## 2.1 Assessment of amber origin based on FTIR analysis

Taking into account the lack of referential with respect to ascription of amber origin, and considering as critical issue the transformation occurring on amber samples during historical ages strongly influenced by the storing conditions in the deposits where were discovered, in the attempt of establishing few definite FTIR criteria to be useful for amber origin proper assignment we started the analysis not directly with archaeological samples but first, with geological amber, of controlled and certified origin, both from Baltic sources and from Romanian sources. Further obtained results are detailed.

### 2.1.1 FTIR method

FTIR assays of amber were performed using the FTIR-VAR technique with a beam incidence angle of  $45^\circ$ , on a Bruker TENSOR 27 instrument, using the OPUS software version 6.0. The samples were used without any pre-treatment, as whole pieces fixed on a gold mirror, and all the spectra were registered versus a background of clean gold foil between 4000 and 600  $\text{cm}^{-1}$ . The spectral resolution was 4  $\text{cm}^{-1}$ , and the co-added scans 96, with an aperture of 4 nm. The FTIR-VAR technique is able to provide the same information as FTIR in terms of transmittance, with a slight loss in signal intensity, but with the advantage of preserving samples integrity. In addition, the bounds between atom plans are not destroyed, and, as consequence, the amount of provided information increases.

### 2.1.2 Geological amber FTIR assessment

A large lot of samples from different controlled origins were analysed by FTIR-VAR, from Romania (Colți, Buzău County), from the Baltic region (Palanga and Kaliningrad), from Germany and Poland in order to settle a certain pattern to differentiate Romanian amber from other types of amber, especially the Baltic variety (the material was provided, mainly, from the National Geological Museum from Bucharest). In the case of unsure observations, to clarify some spectral zone from the fingerprint region (1300-900  $\text{cm}^{-1}$ ), or the region 1800-1450  $\text{cm}^{-1}$ , the transmittance spectra of the samples were used for a better evaluation. Spectra were analysed and assigned on the three wave-numbers domains of significance for amber, namely those between 3600-2000  $\text{cm}^{-1}$ , 1820-1350  $\text{cm}^{-1}$  and the 1250-1045  $\text{cm}^{-1}$  regions, which correlate with hydroxyl groups, carboxyl groups, carbonyl groups and with C=C instauration.

Subsequent data acquisition the following observations were drawn:

- a. There are no notable differences between Romanite spectra and Baltic spectra in the 3600-3000  $\text{cm}^{-1}$  region mainly in case of geological samples. The noteworthy differences

appear (as in any IR technique) in the 'Baltic shoulder' region, 1250-1060  $\text{cm}^{-1}$ , and in the 1161-1155  $\text{cm}^{-1}$  region. For the Baltic amber, the shoulder appears in the region 1275-1155  $\text{cm}^{-1}$ , while that of Romanite has a different shape and is shifted to about 1045-1020  $\text{cm}^{-1}$ , as may be noticed from Fig. 1.

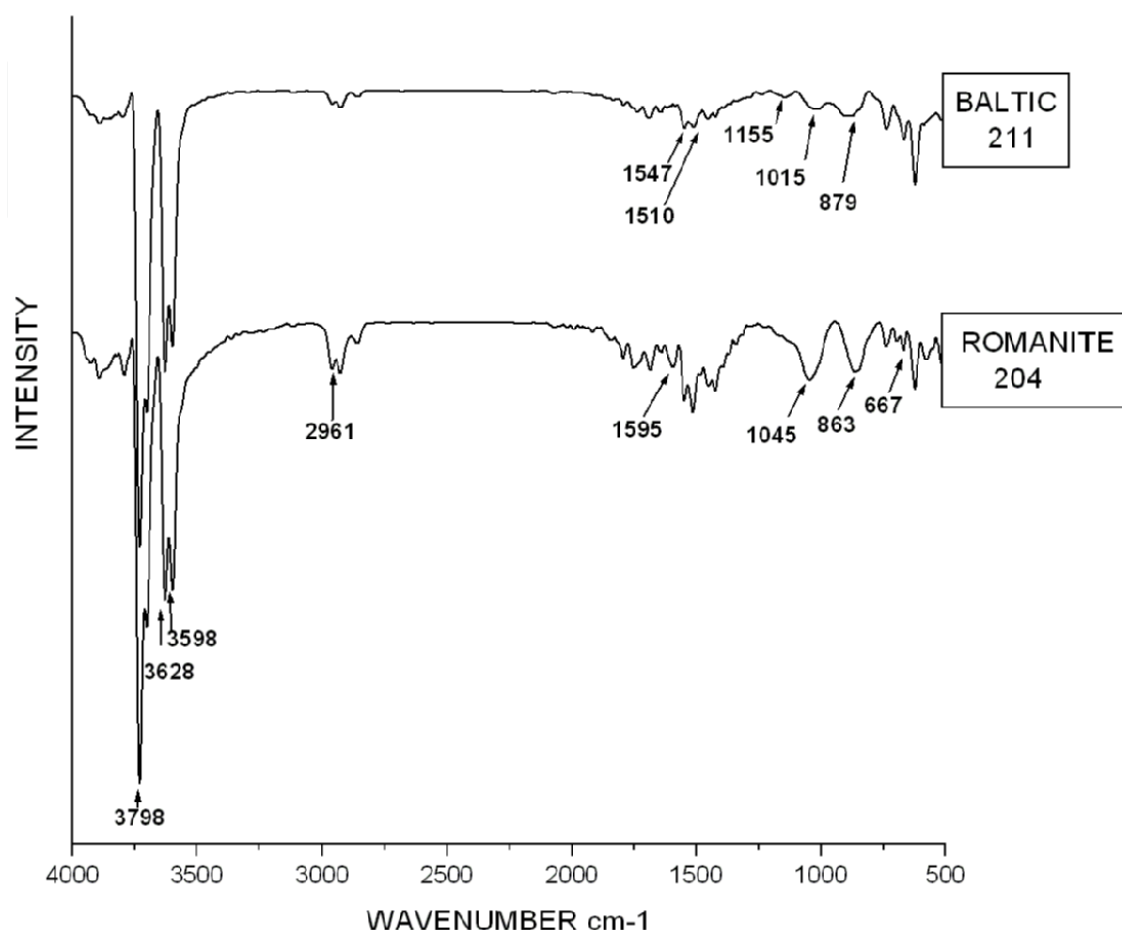


Fig. 1. The overlaid FTIR-VAR (reflectance) spectra, region 4000-600  $\text{cm}^{-1}$  for geological reference Baltic amber (211) and reference Romanite (204)

- b. An important difference in Variable Angle Reflectance spectra is registered for absorption bands from 900-600  $\text{cm}^{-1}$  region (Fig. 1); in this region two species can be differentiated, depending on the age of the polymer. The absence of some characteristic bands indicates that the contraction-reticulation of the polymeric chain is finished (connected with the older age of fossil resin); the absence of a double peak at 667  $\text{cm}^{-1}$  in the Baltic amber spectra and the appearance of the shifted shoulder toward 1045  $\text{cm}^{-1}$ , in the case of Romanite when compared to the Baltic shoulder, that occur at higher wavenumbers (demonstrated also by Fourier spectra de-convolution) provided evidence that Romanite was formed after Baltic amber (*i.e.*, it is younger), as it may be observed in Fig. 1.
- c. There are vibration frequency shifts determined by the degree of ethers and esters formation, correlated to the number of functional groups from the chain and showing evidence on the intramolecular bounds, which appear frequently in amber type resins with younger ages (for example the OH group, specific to Romanite, is slightly shifted

- due to intramolecular hydrogen bonds toward  $1595\text{ cm}^{-1}$ , if compared to the Baltic amber where it occurs about  $1640\text{ cm}^{-1}$ ).
- d. The amber has an amorphous structure, and as consequence the reproducibility of determinations is affected by the heterogeneity of the sample, the obtained spectra depending on the analysed part of the sample. As a result of these observations, for each sample were registered two spectra, for different zones of sample, in order to observe if significant differences appear between the two, due to appearance/disappearance of certain absorption bands (specific vibration frequencies of interest). It was observed that difference between two spectra of the same sample appear only in the spectral region related to methyl, methylene, *etc.* ( $-\text{CH}_3$ ,  $-(\text{CH}_2)_n$ ,  $-\text{CH}$ , *etc.*) chains, namely  $2962\text{--}2850\text{ cm}^{-1}$ , and for the specific tensile bands of  $\text{CH}_3$  from  $1375\text{ cm}^{-1}$ . This led to the conclusion that the presence of functional groups (which are important because they correlate with the origin and the age of the sample, and giving the sample specificity) are equally distributed. Therefore it could be considered that the analytic information supplied by FTIR is acceptable, since the wavenumbers corresponding to carboxylic chains and hydroxy-carboxylic acids at  $1547\text{--}1423\text{ cm}^{-1}$  for Romanite and, respectively,  $1547\text{--}1300\text{ cm}^{-1}$  for Baltic amber are preserving their region for each duplicate recorded spectrum.

The differences appearing in the  $1684\text{--}1642\text{ cm}^{-1}$  band of Baltic amber with respect to the  $1547\text{ cm}^{-1}$  band of Romanite are determined by the shift of asymmetric vibration frequencies for the carboxylic type groups, as a function of the length of hydrocarbon chains. A strengthening-ageing of polymeric chains leads to shifts toward smaller wavenumbers. This can be observed also in  $1046\text{--}900\text{ cm}^{-1}$  region, where the shifts toward the smaller wavenumbers are related to the better confirmation of the Baltic origin. The significant regions for each type of amber are summarised in Table 1, corresponding comment with respect to archaeological amber spectra being introduced at this point for a better understanding of the noticed differences.

### 2.1.3 Archaeological amber FTIR assessment

After analysis of geological specimens of amber, the next step was devoted to archaeological samples analysis. The investigated samples were originated from different times (Neolithic, Bronze Age, Roman Age, Byzantine period, *etc.*) found on different archaeological sites from Romania.

Concerning the archaeological samples, the FTIR-VAR spectra pointed out some differences between the archaeological and geological material. Archaeological samples most generally presented a less intense signal in the  $3600\text{--}3000\text{ cm}^{-1}$  region, which correlates with  $-\text{OH}$  groups and influence the H bonds (Fig. 2); the presence of  $-\text{OH}$  groups was confirmed by a signal of lower intensity for archaeological samples in the  $746\text{--}736\text{ cm}^{-1}$  region, especially for Baltic amber, the relative dehydration of archaeological samples as compared to geological materials being the probable cause (Fig. 2).

The fingerprint zone is different in most of archaeological samples in comparison with geological ones. This region presents adsorption bands of higher intensity for the majority of archaeological samples and some shifts of the specific wavenumbers take place (Figs. 2-3).



Sample of controlled origin (geological)	Wavenumber domain (cm <sup>-1</sup> )	Signal Assignment	Comments regarding the differences between geological and archaeological spectra
Romanian amber (Colti, Buzău County)	3893-3200	OH frequencies, alcoholic (phenolic free OH and bound intramolecular OH) from hydroxy-acids; observed wavenumbers shifts characteristic of amorphous structures.	Less intense signals in this region for archaeological samples and slight shifts
	1684-1600	C=C; C=O frequencies of bond vibrations; out of plane vibration of bonded C-H-C. Plane vibration of H bonds (to O). Assignment confirmed by the peaks from 620-750 cm <sup>-1</sup> domain. 1600-1604 -COO-unsaturated from carboxylic acids;	More intense signals in archaeological samples
	1617	OH group, specific to Romanite, that usually occurs as wide band at 1595 cm <sup>-1</sup> , shifts and appears as shoulder toward 1617 or respectively 1625, due to H intramolecular bonds.	Not always present in archaeological samples
	1547-1423	Specific for carboxylic chains and hydroxy-carboxylic acids;	More intense signals in archaeological samples, shifts
	1046-doublet	Specific peak OH & C=O, slightly shifted due to intramolecular bonds.	
	750-620	Out of plane vibrations of C=O; combined bonds with those specific to C-C=O	
Baltic amber (Bitterfeld, Germany)	3893-3200	Same assignment as above, the differences appear in intensity and slight shifts, due to the different number of intramolecular bonds with respect to those of Romanite;	Less intense signals in this region for archaeological samples and slight shifts
	1684-1600	Same assignment as above, the differences appear in intensity and slight shifts, due to the different number of intramolecular bonds with respect to those of Romanite	More intense signals in archaeological samples, shifts
	1547-1300	Same functional groups, carboxylic chains and hydroxyl-carboxylic acids;	
	1155-1275	Baltic shoulder	Not always present in archaeological samples
	1046/1001	Very well defined peak of OH & C=O; compared to 1046-doublet of Romanite, has different shape and is shifted toward smaller wavenumbers in Baltic amber	More intense signals in archaeological samples, shifts
	750-620	Single peak, sharp, intense, specific for C-O, region slightly different in shape compared to Romanite	Not so well defined in archaeological samples

Table 1. The main characteristics of spectral domains in Baltic amber and Romanite and comparison between geological and archaeological samples)

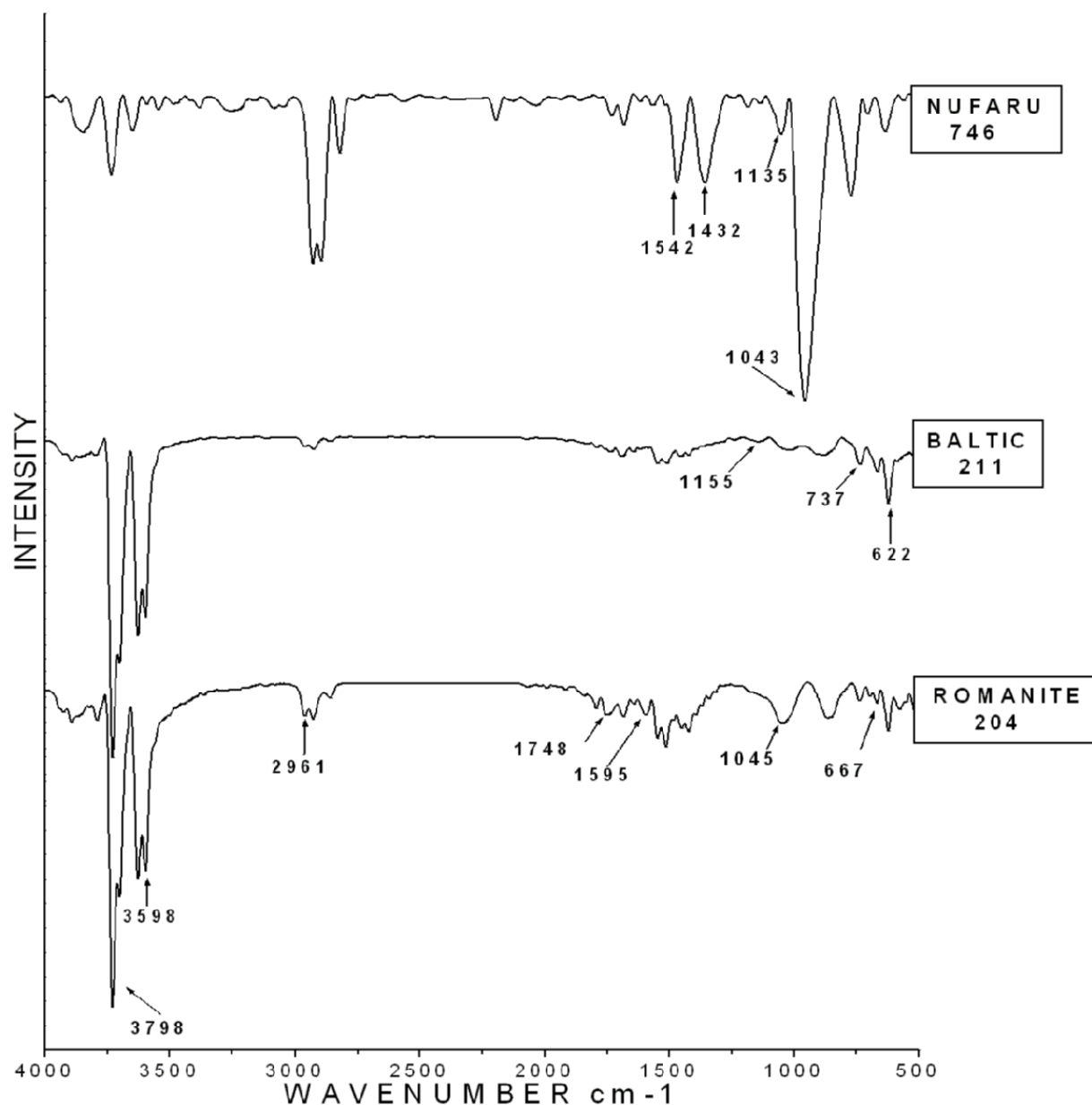


Fig. 2. The overlaid FTIR-VAR (reflectance) spectra, region 4000-600  $\text{cm}^{-1}$  for geological reference Baltic amber (211), reference Romanite (204), and an archaeological sample from Nufăru (746)-Byzantine period- assigned by us to Baltic origin

Another difference in VAR spectra of geological origin is registered for absorption bands from 800-600  $\text{cm}^{-1}$  region: 622-621  $\text{cm}^{-1}$  are ascribed to C-O, C=O out of plane bands; 746-736  $\text{cm}^{-1}$  are the confirmation of OH and H bonds; 676-666  $\text{cm}^{-1}$  are the confirmation of  $\text{CH}_2$  bonds. The absence of a double peak at 667  $\text{cm}^{-1}$  in the Baltic amber spectra indicates that the contraction-reticulation of the polymeric chain is complete (an aspect related to the older age of the fossil resin, in our case the Baltic species). This region is not so well defined in archaeological samples, especially for Baltic amber (Figs. 2 and 3).



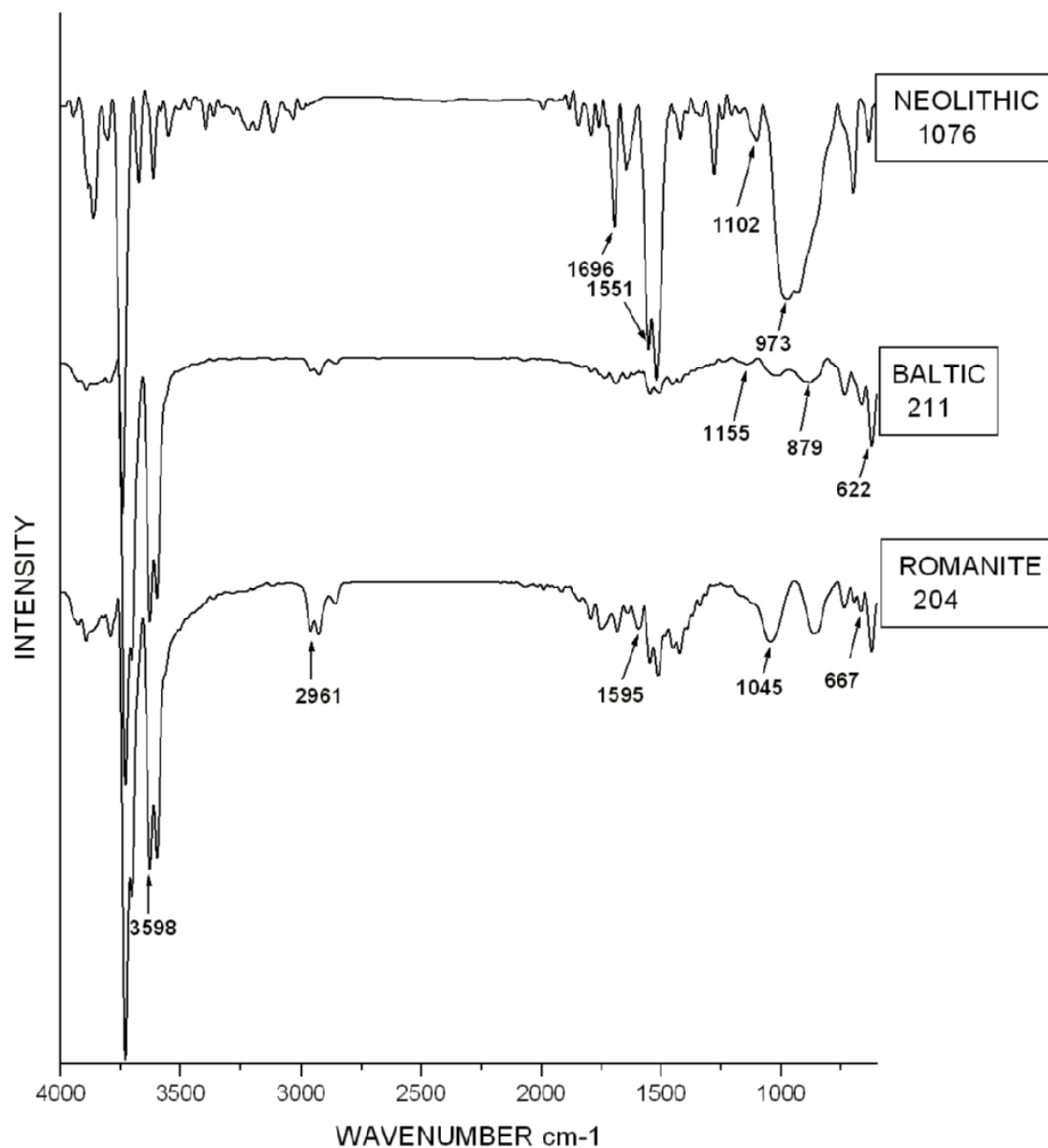


Fig. 3. The overlaid FTIR-VAR (reflectance) spectra, region 4000-600  $\text{cm}^{-1}$  for geological reference Baltic amber (211), reference Romanite (204), and an archaeological sample from Pitesti (1076) –neolithic period- assigned by us to Baltic origin

Based on the relative comparison with the geological reference material (both Baltic and Romanian amber, see Table 1) and according to the FTIR-VAR bands of archaeological samples from the region 1820-1350  $\text{cm}^{-1}$ , 1275-1020  $\text{cm}^{-1}$  and 900-600  $\text{cm}^{-1}$ , the classification of several archaeological samples is summarised in Table 2. Some spectra obtained for the samples from Nufăru (Roman Age), Cioclovina (Bronze Age) and a Neolithic bead are presented in Figs. 2, 3 and 4.

Sample origin	Age	FTIR-VAR assignment
Grădistea-Cotlogeni, one bead Pitesti, one bead (2 samples)	Neolithic	Baltic amber (unpublished)
Cioclovina hoard, 12 beads (43 samples)	Late Bronze	10 beads Romanite 2 beads Baltic amber (Teodor ES et al., 2010)
Rosia Montană, statuette (6 samples)  Dobrogea region (Tomis, Callatis, Beroe, Carsium, Noviodunum) 25 beads (85 samples)	Roman	Baltic amber  16 beads Baltic amber 9 beads Romanite (Vîrgolici et al., 2010b)
Nufăru One pectoral cross, 2 beads (5 samples)	Byzantine	Baltic amber

Table 2. The main categories of archaeological samples analyzed by FTIR-VAR and the assignment of amber origin in comparison with geological samples

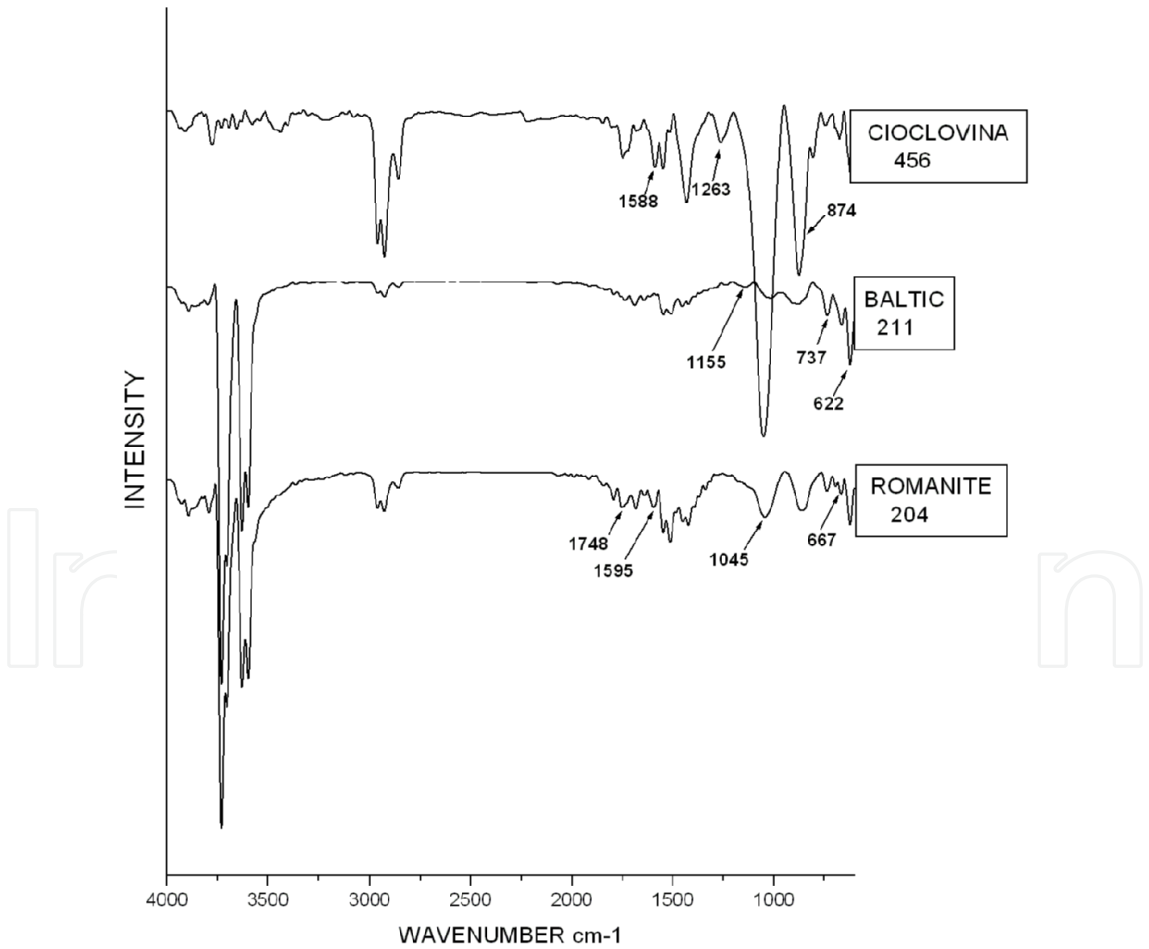


Fig. 4. The overlaid FTIR-VAR (reflectance) spectra, region 4000-600 cm<sup>-1</sup> for geological reference Baltic amber (211), reference Romanite (204), and an archaeological sample from Cioclovina (456)-Bronze period- assigned by us to Romanian origin

These results based on comparison of FTIR-VAR spectra about origin of amber artefacts were clarified and confirmed by other non-destructive analysis (Raman, statistical analysis) and supported by historical context, in some cases. In other cases, the assignment of samples to Baltic amber or local (Romanian) amber contributed to understanding of archaeological (historical) context.

FTIR-VAR is a reliable tool for non-destructive investigating of amber. The spectra are more complex than FTIR-transmittance spectra, the obtained signal are rather highly difficult to ascribe and the variability of results is high, but coupled with statistical analysis and corroborated with other techniques (Raman spectroscopy, X-rays fluorescence) is a consistent method to diagnose the origin of amber in archaeological artifacts.

### **3. Applicability of Fourier Transform Infrared technique in the assessment of bio-mimicking systems. Case study- Human low density lipoproteins**

In order to sustain the assertion regarding the FTIR versatility as non-destructive analytical technique able to provide valuable information with respect to noteworthy molecular changes, the second exemplification is based on assessment of significant bio-markers used to indicate oxidative modifications occurring on cellular membrane. At the level of living organisms the cellular membranes are the main targets for reactive oxygen species (ROS) and reactive nitrogen species (RNS). Both ROS and RNS induce lipid peroxidation (LPO) of unsaturated fatty acids from membrane phospholipids. At the cellular level, reactive species are responsible for changes in the membrane properties, inducing modification on cell permeability and enzyme activities (Ahsan et al., 2003).

In our experiments we developed a bio-mimetic to be applied in assessment of lipoperoxidation processes using as significant oxidative substrate a component of the cellular membrane, low-density lipoproteins. The system development was based on system depositing a thin lipoproteic layer on the surface of conductive solid support, usually gold sheet, and quantification of the lipoprotein peroxidation degree by electrochemical measurements, the intensity of the registered intensity current at the lipoperoxides specific peak potential being proportional with the amount of formed lipoperoxides. At this point have to be mentioned the fact that we employed the VAR-FTIR in analysis of structural modifications occurring to low-density lipoprotein as result of the oxidative changes induced by free radicals (ROS) attack.

#### **3.1.1 FTIR method**

Starting from the important experimental issue which states that an appropriate development of a bio-mimetic system by immobilization of a compound to a support preserves the structure of the immobilized compound, the first FTIR study was performed on low-density lipoprotein layer deposited on gold support, the results being compared to those obtained for un-bounded lipoprotein. For the deposited layer the reflectance mode was employed, while for free lipoprotein the transmittance mode was used. FTIR spectra were recorded at room temperature using a Bruker Tensor 27 Fourier Transform spectrometer. The spectra were collected and ascribed using Opus software. In transmittance mode the spectral range was 4000 – 400  $\text{cm}^{-1}$ , the aperture 4 cm, the spectra resolution 4  $\text{cm}^{-1}$  and 98 scans being acquired for each spectrum, 20 Hz. Samples were pressed into a potassium

bromide (KBr) pellet, the background spectrum being recorded against KBr pellet. In reflectance mode the spectral range was 4000 – 600 cm<sup>-1</sup>, the background being recorded for an unmodified polycrystalline gold sheet after that being recorded the samples’ spectrum. The optimum reflectance angle was 45 degrees, the aperture 6 cm, the spectra resolution 4 cm<sup>-1</sup>, 98 scans being acquired for each spectrum, with 2.2 Hz.

3.1.2 FTIR assessment of native and oxidised low-density lipoprotein

As mentioned in the previous section, the first FTIR studies were performed to evaluate the suitable deposition of the low-density lipoprotein on the gold support in order to preserve the lipoprotein structural characteristics. This is an important experimental issue, because the protein structure and surface charging are the most important structural features necessary to be maintained to ensure feasible “ex-vivo” analytical information with respect to oxidative changes induced on cellular membrane by ROS.

The main regions corresponding to FTIR absorption bands and specific for native LDL are given in table 3. Absorption bands from 2800–3000 cm<sup>-1</sup> corresponding to methyl groups are well defined, no matter the type of the sample, either free or deposited LDL.

Wavenumber domain (cm <sup>-1</sup> )	Signal assignment	Comments and observations
2800-3000	CH <sub>2</sub> – symmetric and asymmetric stretching vibration, CH <sub>3</sub> – asymmetric stretching vibration	2927 cm <sup>-1</sup> (v <sup>as</sup> <sub>CH2</sub> ), 2854 cm <sup>-1</sup> (v <sup>s</sup> <sub>CH2</sub> ), 2954 cm <sup>-1</sup> (v <sup>as</sup> <sub>CH3</sub> ) and 2866 cm <sup>-1</sup> (v <sup>s</sup> <sub>CH3</sub> ) are specific for lipid chains
1740	C=O – stretching vibration for ester group of lipids	-
1630-1680	C=O – stretching vibration for carbonyl group for protein, amide I	1656 cm <sup>-1</sup> band correspond to amide I helix structure being the result of 60% vibration of C=O group and 20% vibration of N-H
1541	N-H – deformation (scissoring)vibration for amine group of protein, amide II	Is due to 60 % vibration of N-H bound and the rest from -CO-NH- functional group
1466	CH <sub>2</sub> – deformation vibration for methylene group	-
1170-1245	PO <sub>2</sub> <sup>-</sup> – asymmetric stretching vibration for phosphate groups	-
1063-1100	PO <sub>2</sub> <sup>-</sup> – symmetric stretching vibration for phosphate groups CO-O-C vibration for esters groups	Studies performed on incidence angles different of 45° proved that ester groups are oriented preferentially at 75°, the intensity of the corresponding band at 1099cm <sup>-1</sup> increasing suddenly

Table 3. Main IR absorption bands of low-density lipoprotein

As observable from figures 5 and 6, the amide specific band absorptions for proteins, amide I band around  $1654\text{ cm}^{-1}$  and amide II band around  $1541\text{ cm}^{-1}$  (Firth et al. 2008; Banuelos et al. 1995) are not changed when LDL was deposited on the gold support. This observation is important because it proved that the secondary structure of protein is preserved subsequent deposition therefore it can be concluded that the deposition on solid support did not affect the LDL functionality, and, consequently, that deposited LDL is expected to react with free radicals according to the same pathway as free LDL. Moreover, it should be mentioned that this argument is consistent with the data published by Paker (Paker, 1991) where it is mentioned that LDL *ex vivo* peroxidation pathway is similar as *in vivo* peroxidation pathway.

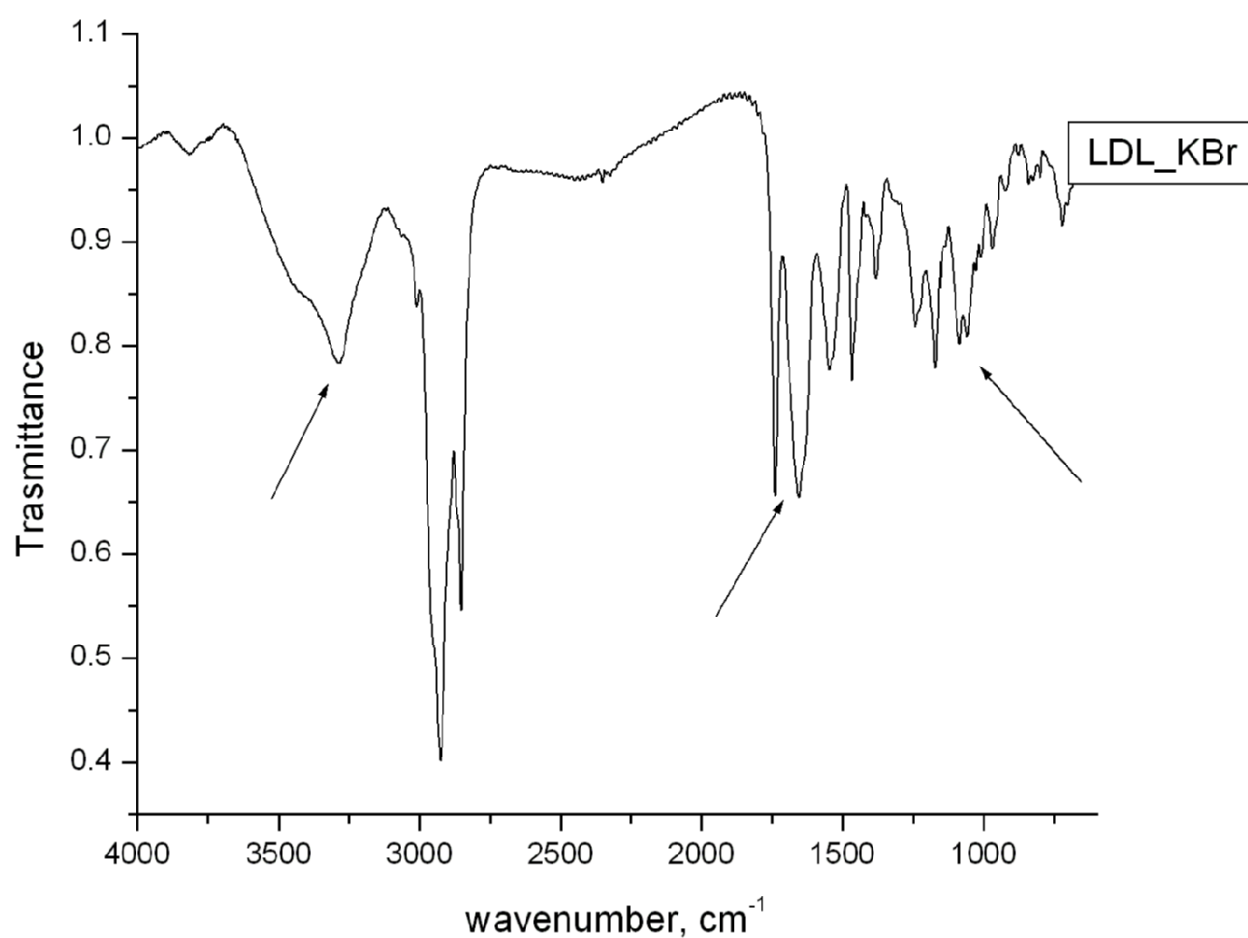


Fig. 5. FTIR spectra of LDL free, on transmittance (KBr pelleted)

When lipoprotein are subjected to the attack of peroxy radicals, thermally induced from aqueous solutions of azo-initiator 2,2'-azobis (2methylpropionamidine).dihydrochloride (AAPH), the lipoperoxidation occurs according to a radical pathway (Litescu et al, 2002; Tache et al., 2011) leading to lipo-peroxides formation on the LDL layer. In our experiments the FTIR analysis was performed first on the LDL deposited on the solid support, then the LDL was subjected to free radicals attack for 10 minutes, allowed to dry on inert atmosphere and after that the oxidised LDL layer was once more assessed by FTIR.

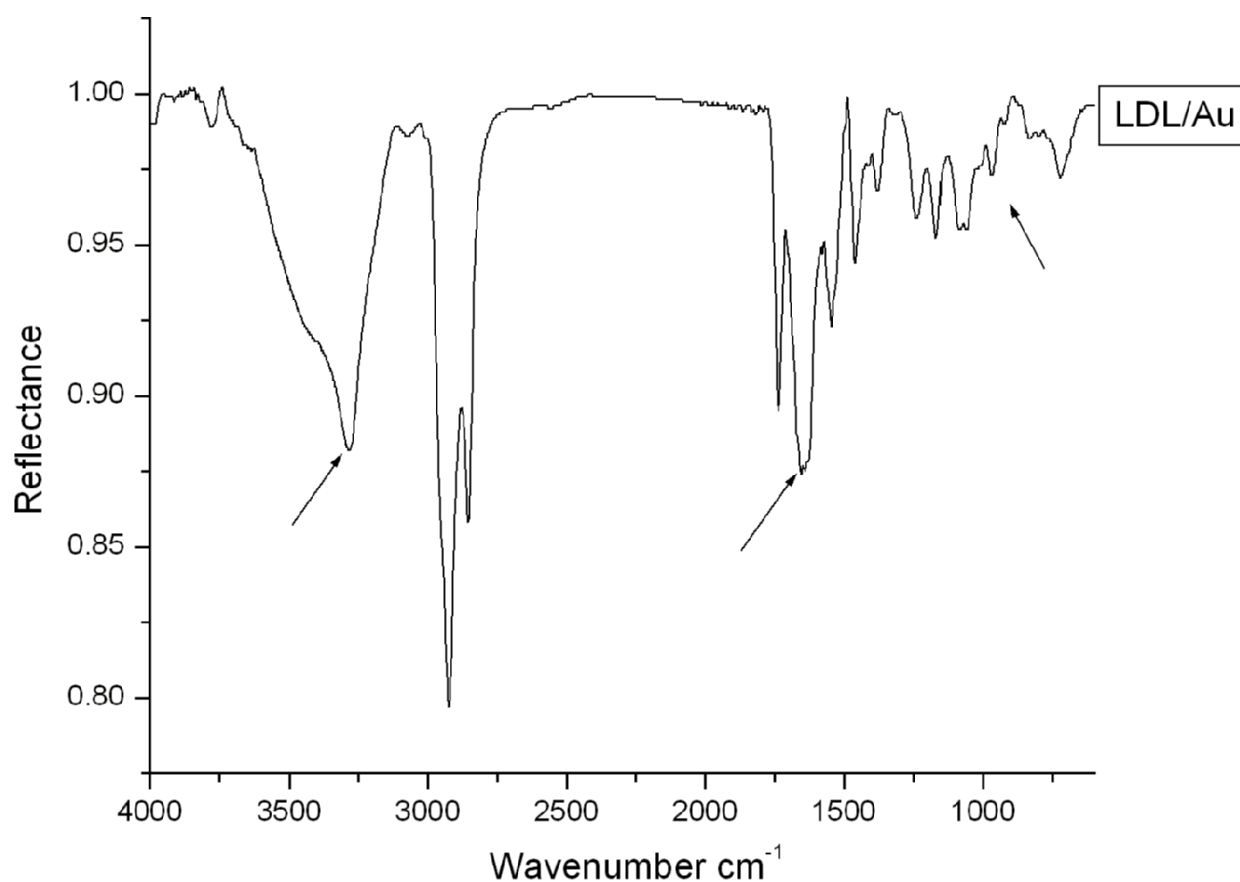


Fig. 6. FTIR spectra of LDL on Au support (variable angle reflectance, incidence angle 45°)

The performed studies proved that in the presence of free radicals (Fig. 7), the IR absorption bands corresponding to ester groups from lipid residues at 1740 cm<sup>-1</sup> were changed in intensity and shifted as wavenumber, thus proving the lipoperoxides formation.

Another proof of lipoperoxides existence was the presence of HO absorption bands from 3600–3700 cm<sup>-1</sup> and 917 cm<sup>-1</sup>. In detail, the signal ascription are as follows: the band from 3278 cm<sup>-1</sup> increasing in intensity and shoulders rise at 3334 cm<sup>-1</sup>, 3304 cm<sup>-1</sup>, 3220 cm<sup>-1</sup> and 3197 cm<sup>-1</sup> assigned to O-H and N-H vibrations. The bands from 3072 cm<sup>-1</sup> are corresponding to hidroxil and amine groups involved in hydrogen bonds. In the same time, it is important to mention that several changes arose around 1717 cm<sup>-1</sup> indicating the formation of new C=O groups.

The changes observed on FTIR spectra of deposited LDL correlated perfectly with electrochemical and MALDI information (Litescu et al, 2011), proving the usefulness of non-destructive FTIR analysis in ascribing the oxidative modification occurring on lipoproteic components of the cellular membrane.



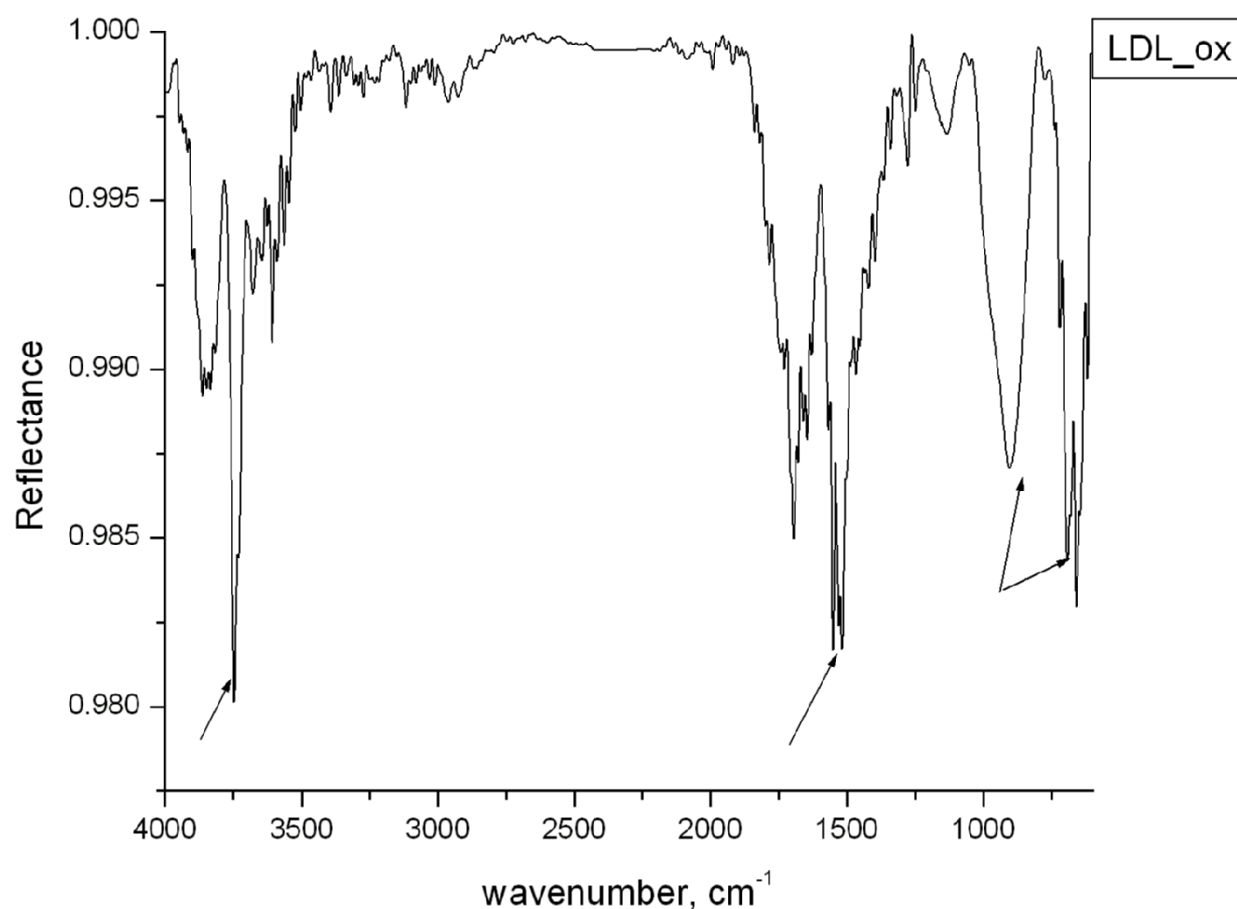


Fig. 7. FTIR spectra of native peroxidised LDL deposited on Au support

#### 4. Conclusions

The use of FTIR, especially as variable angle reflectance technique, proved to be of crucial importance in two main types of applications where the critical issues are the importance to conserve the sample integrity and the limited amount of available sample.

Two examples of FTIR non-destructive analysis employment in two very different research domains, archaeology and modified surfaces are supporting the highest utility of the technique when the analysis is dealing with valuable samples, sometimes of patrimony value, which have to remain un-affected subsequent analysis, as it was the amber samples case study, or when the analysis have to provide arguments on sharp and specific structural changes, as it was the case of lipoprotein oxidation study.

It could be concluded that FTIR proved its efficiency in evaluation of the oxidative modifications on the level of one of the main components of the cellular membrane, oxidative process which plays, generally, as key-event in several age -related and degenerative pathologies.

In the same time, it should be emphasized that, in our opinion, FTIR-VAR technique use as non-destructive way to analyse archaeological artefacts is strongly recommended, especially when coupled with statistical analysis.

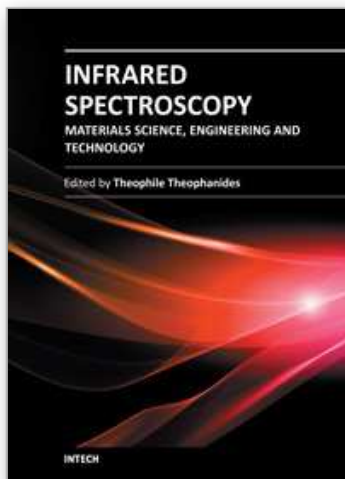
## 5. Acknowledgment

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The present book is a definitive review in the field of Infrared (IR) and Near Infrared (NIR) Spectroscopies, which are powerful, non invasive imaging techniques. This book brings together multidisciplinary chapters written by leading authorities in the area. The book provides a thorough overview of progress in the field of applications of IR and NIR spectroscopy in Materials Science, Engineering and Technology. Through a presentation of diverse applications, this book aims at bridging various disciplines and provides a platform for collaborations among scientists.

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