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INTERNATIONAL SYMPOSIUM
"AMBER. SCIENCE AND ART"

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# AMBERIF 2018

International Fair of Amber, Jewellery and Gemstones

# INTERNATIONAL SYMPOSIUM AMBER. SCIENCE AND ART

# Abstracts

GDAŃSK, POLAND

22-23 MARCH 2018

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# Foreword

For 25 years, AMBERIF has been gathering people of common passion: Baltic amber (=succinite). Since its first edition, AMBERIF has been accompanied by scientific seminars, which were initiated by Prof. Barbara Kosmowska-Ceranowicz and Wiesław Gierłowski. In its silver jubilee year 2018, the seminar is an International Symposium, organized under the supervision of AMBERIF Project Director Ewa Rachoń.

Science and art have been coming together from times immemorial. They are like a good marriage, supporting and complementing each other, providing creativity and inspiration, opening new perspectives and opportunities every day. Baltic amber, but also other fossil resins of the world, is a perfect example of a link between science and art. It is because succinite in a magical way simply attracts—not only those who just love the secret beauty of amber, but also scientists and artists.

During the two days of the Symposium (22-23 March 2018), we would like to present, in light of the latest scientific reports, the dynamic development and progress of the research areas related to amber in the field of natural sciences, exact sciences and humanities. Four thematic sessions, which will be chaired by members of the Scientific Committee of the Symposium, with the honorary Chair of the Symposium, Professor Barbara Kosmowska-Ceranowicz (Museum of the Earth in Warsaw, Polish Academy of Sciences), include lectures and poster sessions. Our invitation as keynote lecturers was accepted by: Prof. Faya Causey (Getty Research Institute, USA), Prof. Sarjit Kaur (Laboratory of Amber Research, Faculty of Chemistry, M. Vassar College, USA), Prof. Joseph B. Lambert (Faculty of Chemistry, University of Trinity, USA), Prof. Vincent Perrichot (Faculty of Earth Sciences, University of Rennes 1, France).

Session *"Life traces in amber"* chaired by Prof. Jacek Szwedo and Dr Elżbieta Sontag (Faculty of Biology, Laboratory of Evolutionary Entomology and Museum of Amber Inclusions, University of Gdańsk) is dedicated to the traces of ancient organisms and their activities, preserved in fossil resins. Its main topic is the inclusion of insects and other arthropods, plants, fungi and other organisms. This session is also a celebration of the 20th Anniversary of the Museum of Amber Inclusions at the University of Gdańsk.

Local and supra-regional traditions in the manufacture of amber objects among European societies of the Bronze and Iron Age is the leading topic of the session *"Stylistics and processing technology of amber products in 3rd-1st millennium BC: local and interregional perspective"* conducted by Prof. Janusz Czebreszuk and Mateusz Cwaliński (Institute of Archaeology, Adam Mickiewicz University in Poznań). The twelve oral communications presented in this session will be summarized in a special final discussion.

The latest achievements in research on amber properties with the use of modern research techniques and applications of these achievements form the main topic of the session *"Highlights of amber properties investigations and current aspects of amber mining."* This part of the Symposium is also dedicated to very important current problems—also environmental ones—related to the geology and extraction of amber. This session is under the supervision of Dr Ewa Wagner-Wysiecka and Dr Natalia Łukasik (Faculty of Chemistry, Gdańsk University of Technology).

The amazing and captivating world of myths, toposes and their representations in amber artefacts is the subject of the session on *"Myths, collections and conservation of amber,"* led by Dr Anna Sobecka (Faculty of History, University of Gdańsk).

Instead of a summary—

***"Man is unique not because he does science, and he is unique not because he does art, but because science and art equally are expressions of his marvellous plasticity of mind"*** (Jacob Bronowski)

***Ewa Wagner-Wysiecka***

III millennium BCE. In the second half of this millennium, diversification in amber supply sources seems to occur: Baltic amber is traded for the first time and local Cretaceous amber is exploited again (Odriozola et al. 2017).

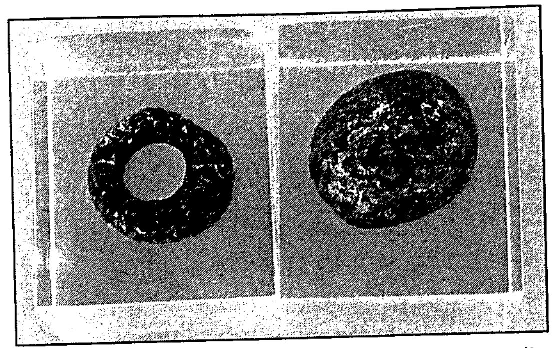

**Fig. 1.** Anular and biconical amber beads – Tomba a grotticella n. 3 of the necropolis of Laterza (Eneolithic – second half III mill. BCE) – National Archaeological Museum of Altamura, Italy.

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# Investigating the degradation of Baltic amber

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## Introduction

A recent survey of the National Museum of Denmark's (NMD) collections revealed more than 17,000 unique pieces of Baltic amber in the form of beads, jewelry and other decorative pieces, making it one of the largest collections of amber in Europe. After its use as jewelry or other decorative pieces in pre-history, amber is likely to be buried for many years in dry or wet, boggy soils or transported in seawater before discovery. The survey concluded that 45% of amber in NMD's collections exhibited signs of deterioration, manifested by surface crazing, powdering and discoloration (see Figure 1). Based on surface appearance alone, the condition of the objects seemed to reflect the environments in which they were found. Only 4% of those amber pieces that were excavated from wet bogs or found in water exhibited a high degree of degradation compared with 40% of objects found in dry environments. Amber found in dry soils were frequently recognizable by their pale yellow, friable, surface crusts. By contrast, amber found in wet environments was dark brown in colour with cohesive surfaces. Because the amber collections reflect the economic, social, religious and other cultural beliefs prevalent in pre-historic Europe, it is essential that they are preserved for study and enjoyment by future generations.

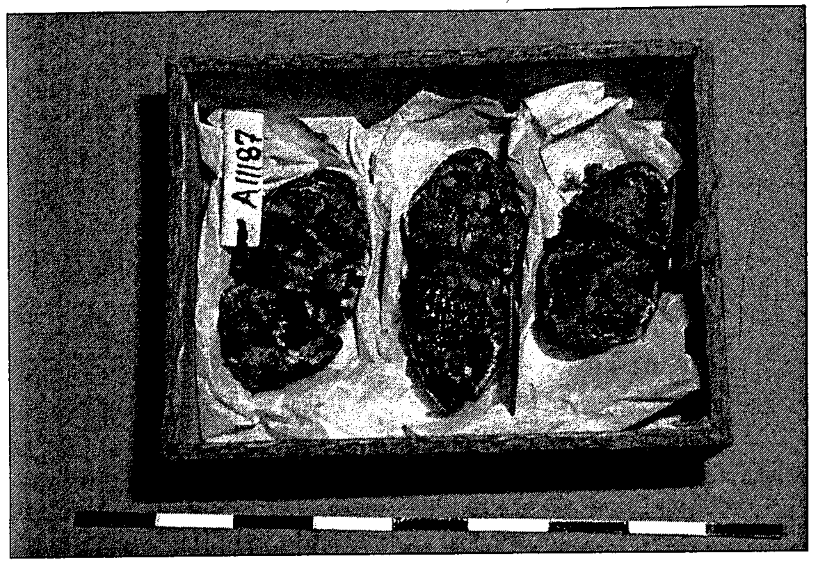


**Fig. 1.** Amber beads from the Stone Age exhibiting typical surface crumbling, disintegration and discoloration. The objects are from the collections of the National Museum of Denmark.

Identifying the pathways and rate-controlling factors associated with degradation are the first steps to developing effective conservation strategies that inhibit chemical breakdown reactions and prolong the useful lifetimes of all heritage materials. However, conducting such studies on museum objects comprising amber poses complex practical challenges. Firstly, amber's long lifetime (millions of years) prevents study of changes to its chemical and physical properties in real time. Secondly, although chemical and physical analyses of degraded amber provide a snapshot of its current state, they do not reveal the pathways or rate of degradation. Thirdly, in order to comply with the International Council of Museums' code of ethics, examinations of registered museum objects are required to be non- or minimally destructive thus restricting the amount of original sample material available for experiments (ICOM 2013).

Within this framework, research at NMD has produced models of amber that represent the chemical and physical structure of objects dating from the Stone Age. Model samples were exposed to weathering environments in which oxygen, water, radiation, pH, temperature and time are varied to represent a range of burial, storage and exhibition conditions and the physical and chemical properties of their surface examined throughout the exposure period (Pastorelli 2011 and Shashoua et al. 2005). The purpose of this paper is to review the various techniques used to investigate the degradation of Baltic amber, to discuss the findings and their application to current preventive conservation practices.

**Preparation of model amber samples to represent Baltic amber in museums**

Unprocessed Baltic amber from Kaliningrad was used to prepare models. Kaliningrad is a Russian exclave on the Baltic Sea, located between Poland and Lithuania from which 90% of the world's amber is mined.

Two techniques to prepare models from the unprocessed amber were used. Raw amber was cut into cubes, approximately 10 x 10 x 10 mm and polished while cooling with water to minimize loss of volatiles and generation of free radicals by heating. In order to optimise the homogeneity of material within models, amber cooled with solid carbon dioxide at -78°C was milled to form a fine powder (Pastorelli 2011). Pellets (10 x 2mm) were pressed from the powder.

**Exposure of model amber to burial and post-excavation storage environments**

To induce similar symptoms of degradation in undegraded, model amber to those observed in pre-historic pieces within a convenient time period, samples were exposed to accelerated weathering. Elevated temperature is frequently used to accelerate the ageing or degradation processes in industrial polymers so that their stability can be evaluated within a convenient timeframe. It is assumed that the rate of aging is increased by a factor of 2.ΔT/10, where ΔT is the temperature increase from ambient. This is a mathematical expression of the empirical observation that increasing the temperature by about 10 °C roughly doubles the



rate of many polymer reactions and assumes that the primary degradation reaction is first order with an activation energy of 10.R/log $e^2$, where R is the universal gas constant.

Model amber samples were exposed to thermal ageing in the dark at 70° and 100°C until visible changes were observed. In addition, samples were exposed to microclimates created using combinations of heat, water and pH to examine the influence of water and acidity on their rates of degradation. Microclimates containing different percentages of relative humidity (RH) were created by placing water, pre-conditioned silica gel or nothing in air- and water-tight Pyrex glass flasks (100 mL). Amber samples were added, suspended in nylon nets and the closed containers placed in convection ovens at 70° and 100 °C (see Figure 2) Microclimates containing water had a mean RH of 94.7%, those containing silica gel had a mean RH of 6.5% and empty containers had a mean RH of 33.2%. Microclimates with various pH values were generated by adding commercial buffer solutions to the Pyrex glass flasks comprising citric and boric acids to generate pH 3, 5 and 10.

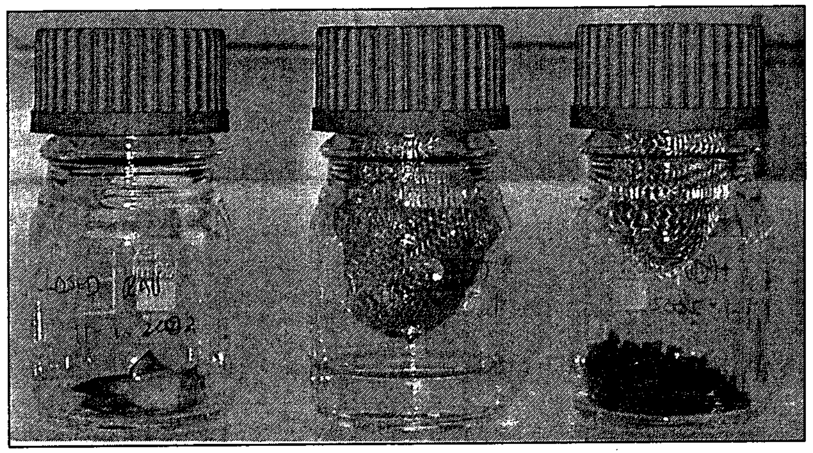

**Fig. 2.** Freshly mined and polished amber exposed to thermal ageing in microclimates containing ambient RH (left), high RH (center) and low RH (right)

Exposure to ultraviolet radiation is known to promote photo-oxidation in amber and is therefore usually excluded from display and storage environments in museums (Beck 1982). However the effect of visible light (380 – 760nm) has been poorly researched. To investigate whether visible radiation accelerated degradation processes in amber, model samples were exposed to light filtered through window glass. This was achieved by subjecting samples to accelerated photoageing using an Atlas Ci3000þ light chamber that delivered wavelengths ranging from 325 nm to 760 nm, emitted by a xenon lamp at an irradiance of

40 $Wm^{-2}$ and illuminance of 88,000 lx at the samples' surfaces. To investigate the influence of combinations of light, water, acid and alkaline environments on the rate of degradation of amber, microclimates containing low and high RH, pH 3, 5 and 10 were created within the Atlas light chamber.

**Examination techniques used to study the degradation of amber**

**Appearance and colour measurement**

Samples were examined visually for changes in surface roughness, cracking and colour change induced by the ageing environment. Colours of model samples before and after thermal and photo-ageing were quantified using a Minolta CM-2600d portable spectrophotometer, fitted with a standard illuminant D65/10° and a diffuse/8° geometry, and including the specular reflection component. Data were expressed using the CIE L*a*b* colour system and colour difference values CIEDE2000 ($\Delta_{00}$) index (CIE 1995 and Luo et al. 2001).

**Attenuated Total Reflectance – Fourier Transform infrared (ATR-FTIR) spectroscopy**

ATR-FTIR spectroscopy was used to quantify levels of degradation present at surfaces of all samples during accelerated thermal and photo-ageing. Spectra were collected over 30 scans at a resolution of $4cm^{-1}$ between 4000 $cm^{-1}$ and 600 $cm^{-1}$ (the lower limit of sensitivity for ATR), using an ASI DurasamplIR single reflection accessory with an angle of incidence of 45° and fitted with a diamond internal reflection element in a Perkin-Elmer Spectrum 1000 FTIR spectrometer. The high refractive index of diamond compared with that of amber (2.4 and 1.5 respectively) allowed absorbance data to be collected from a depth approximately equal to that of the wavelength of the infrared radiation, a maximum depth of approximately 2 microns (Coombs 1999). The quality of spectra depended on intimate contact between the DurasamplIR diamond reflection element and was optimised by polishing amber samples. Identical pressure distribution was achieved for all samples using the pressure device in combination with the torque limiter which allowed the press to be tightened to the same, repeatable level.

Beer's Law, which states that spectral absorbance is proportional to the concentrations of two components in a material, was applied to the spectra. Heights of strong bands at 1730 $cm^{-1}$ assigned to the carbonyl stretch (C=O) and 1448 $cm^{-1}$ assigned to $CH_2$ were determined on raw absorbance spectra and the ratio ($A_{1730}/A_{1448}$) used to quantify degradation (see Figure 3) (Shashoua et al. 2005).

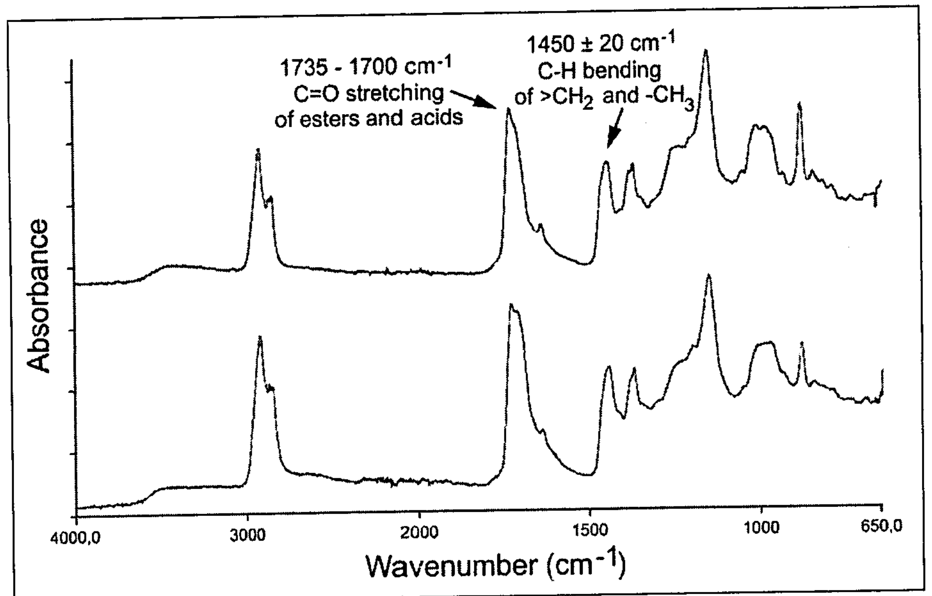


**Fig. 3.** ATR-FTIR spectra of unaged (top) and thermally aged (bottom) Baltic amber. The infrared bands used to quantify oxidation levels of model amber samples are indicated.

**Fourier Transform Raman (FT-Raman) spectroscopy**

Raman spectroscopy is a complimentary technique to FTIR and was also used to quantify degradation, although it should be borne in mind that the infrared radiation examined in Raman spectroscopy penetrates to a deeper level than ATR-FTIR at around 2-3 mm below surfaces.

To minimize the effects of fluorescence exhibited by amber, Raman spectra were obtained with excitation from a Nd:YAG laser at 1064 nm with intensity 350 mW and spectral resolution 4 $cm^{-1}$ on a Bruker RFS 100 FT-Raman spectrometer. Spectra from polished faces of samples and pressed pellets were more intense than those from rough surfaces. Chemical degradation levels were determined from Raman spectra by calculating the ratio between intensity values of C=C stretching and C-H bending, present at 1650-1600 $cm^{-1}$ and 1450 ± 20 $cm^{-1}$ respectively (see Figure 4) (Moreno et al. 2000). A progressive increase in the ratio on ageing indicated formation of new C=C bonds in the amber structure probably due to oxidation while a decrease in ratio was thought to be attributed to depolymerisation.

**Summary of results of examination techniques**

Model samples exposed to thermal ageing appeared to yellow less than those exposed to photo-ageing. Colour measurements supported these observations. Colour difference values ($\Delta_{00}$) ranged from 3 for samples aged at 70°C for 35 days in high RH and 5 at low RH to 8 for samples photo-aged at high RH and 14 at low RH. Colour differences of 1.5 or higher are detectable by eye. These results suggest the presence of both light and RH lower than 50% to maximize discolouration of amber. The effect of acid or alkaline conditions on discolouration was not significant.

ATR-FTIR spectroscopy data showed significantly greater increases in intensities of the absorbance band attributed to carbonyl groups in all the samples exposed to photo-ageing compared with thermal ageing, indicating the rate and extent of photo-oxidation to be higher than that of thermo-oxidation. The increase in concentration of carbonyl groups is likely related to the formation of carboxylic acids. Photo- and thermal ageing in low RH microclimates resulted in a greater increase in the concentration of carbonyl groups (2.25 for thermal ageing), while high RH produced lower concentrations closer to that seen in non-aged amber



(1.45). These results suggest that water either has no influence on the rate of thermo- and photo-oxidation of amber or acts to slow the reaction. ATR-FTIR spectroscopy suggests that the presence of acid or alkaline has no measurable influence on the development of carbonyl groups.

Although FT-Raman spectroscopy showed identical trends between ageing environment and degradation as ATR-FTIR, the magnitude of oxidation shown by Raman was lower in every case. Oxidation was reflected in FT-Raman spectroscopy by a reduction in intensity of C=C bonds in the terpenoid components as they react with oxygen to form carboxylic acids (Pastorelli et al. 2012). Because carbonyl bonds are present only weakly in Raman spectra but strong in ATR-FTIR spectra, the two techniques were complimentary for this investigation. In addition, oxidation that is limited to the upper 2-3 microns of amber samples' surfaces are less likely to be detected by FT-Raman than ATR-FTIR. FT-Raman did not show significant degradation patterns for amber exposed to acidic and alkaline atmospheres.

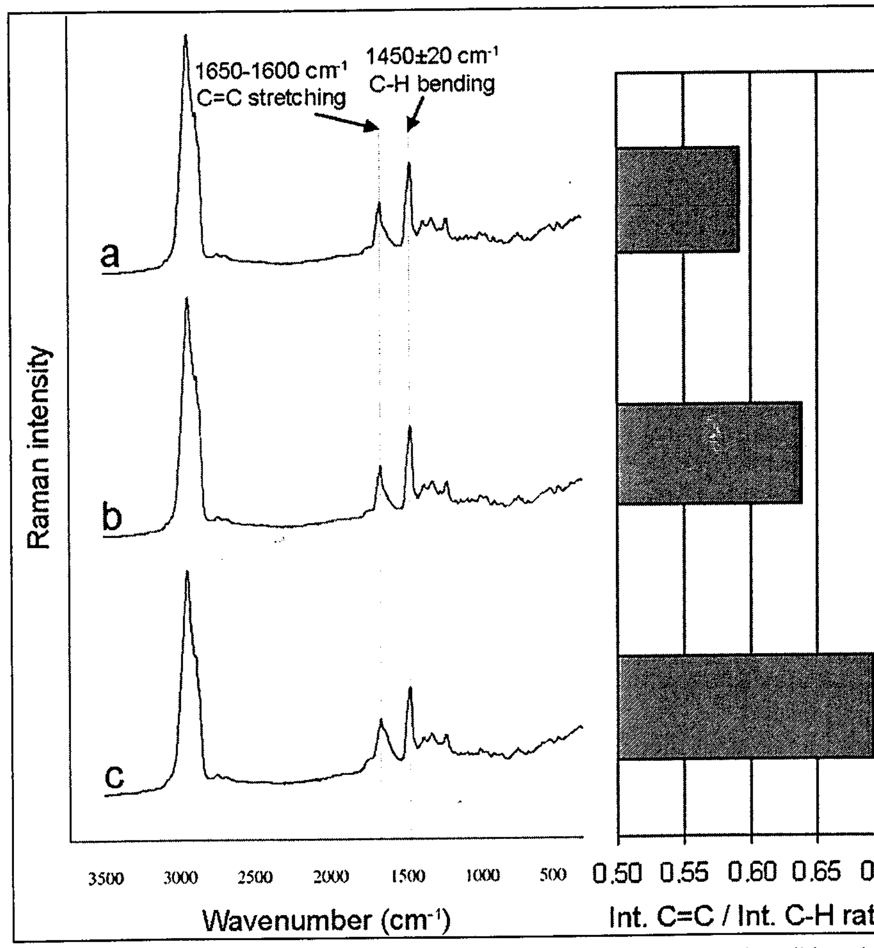


**Fig. 4.** FT-Raman spectra of model amber samples unaged (a), thermally aged for 35 days (b) and thermally aged for 70 days (c). Two vertical lines are plotted at 1625 $cm^{-1}$ and 1450 $cm^{-1}$ to highlight the infrared bands used to quantify degradation levels. Olefinic bonds concentrations for each thermal ageing period are showed on the right. Error is below detection limits.

**Conclusion**

Findings obtained from combining visible examination, colour measurement and spectroscopic investigations of model Baltic amber indicate that the material degrades initially by depolymerisation of the polylabdanoid chains at surfaces (Clifford and Hatcher 1995). The newly-formed C=C bonds undergo oxidation resulting in their conversion to carboxyl acids. As degradation progresses and amber surfaces physically disintegrate, oxygen from air diffuses increasingly deeper into the material and degradation progresses more rapidly than for newer samples. Light and low RH accelerate this process more than heat and the acidity of the surrounding environment have little influence on the rate of oxidation.

Applying the knowledge obtained from studying degradation of model amber samples to preserving amber collections in museums for future generations, it is clear that exposure to daylight, even that filtered by window glass, should be minimized during storage and display. Amber should be stored and exhibited at temperatures as low as practicable with consideration to the comfort of museum guests and storage area personnel. The RH of storage and exhibition environments should be at least 50±2%.

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# Versatile spectroscopic approach in the investigation of cultural heritage objects

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The development of nondestructive and noninvasive analytical procedures, suitable for the provenance study of cultural heritage object made of succinite, and other resins is of utmost importance. It is the most common situation that these investigation do not allowed to take samples that could destroy analyzed fragile objects. Due to the fact only the analysis based on noninvasive, complementary techniques could deliver comprehensive information about investigated objects.

The success of provenance investigation of amber is determined by the adequate choice of the method and the usage of the reference spectra database. To the most widely used spectroscopic methods like Raman and infrared spectroscopy, annihilation spectroscopy (PAS) and scanning electron microscopy with the micro roentgen analysis (SEM-EDS) are applied in the such investigation.

The Raman spectroscopy is recognized as an effective technique used in the provenance investigation of the amber characterized by the opportunity to carry out the in situ measurements without any preparation of the sample. It is quite common that archeological amber objects are covered by the weathered layer caused the strong fluorescence obscuring Raman spectra. Unfortunately, in many cases this outer layer cannot be removed without the damage to the object and implementation of supplementary techniques is



necessary in order to determine the provenance of such amber objects (Łydżba-Kopczyńska et al. 2012). The applicability of the annihilation spectroscopy (PAS) in the analysis of the raw material was proved during investigations of the amber objects discovered in the archaeological excavations (Łydżba-Kopczyńska et al. 2012). Moreover, in the identification of amber are used other spectroscopic methods like: transmission infrared spectroscopy and ATR (Łydżba-Kopczyńska et al. 2015, but they require preparation of samples).

Additional information can be provided by near-infrared reflection spectroscopy in the 800 – 2500 nm spectral range (NIR). As a non-invasive method, it has great potential in the application in sensitive works of art analysis (Klisińska-Kopacz, 2017). In general, it has a greater depth of penetration into the sample than light in the visible range. Near-infrared spectroscopy is based on molecular overtone and combination vibrations. The molecular overtone and combination bands seen in the near-IR are typically very broad, therefore their interpretation is very often not straightforward. However, their unquestionable advantages, such as simple measurement and no need for sample preparation, motivate us to further work on its use in amber objects analysis, also with the help of multivariate chemometric methods (Majda et all, 2016). The access to the adequate database undoubtedly could be considered as the second important condition which lead to satisfying results of investigation.

The Cultural Heritage Research Laboratory at the Faculty of Chemistry, Wrocław University developed the Raman spectra database of amber and copal which was successfully applied in the provenance study of archaeological amber objects discovered in Poland (Łydżba-Kopczyńska et al. 2015, Peris-Diaz). The database is systematically developed and recently was extended to incorporate ATR, annihilation positronium reference spectra, near-infrared reflection spectroscopy (NIR) and also SEM-EDS (Kosmowska-Ceranowicz et al. 2017) data of amber and copal. The developed comparative spectral database is based on reference spectra of fully documented samples of succinite, fossil resins, subfossil resins and imitations from the comprehensive collection of The Museum of the Earth's Amber Department, Warsaw, started in 1951.

The application of the versatile spectroscopic approach in the investigation of cultural heritage objects made of amber will be illustrated by provenance investigation of amber jewelry discovered in the archaeological excavations in Domasław (Łydżba-Kopczyńska et al. 2012), archeological amber objects from the collection of the Archeological Museum in Warsaw, samples originating from the amber deposits discovered in 1906 and 1936, nearby the horse racing track in Wroclaw-Partynice (Ger. Breslau-Hartlieb) (Seger, 1930; Nowothnig 1937) and the amber altar from XVII century belonged to the collection of the National Museum in Krakow.

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