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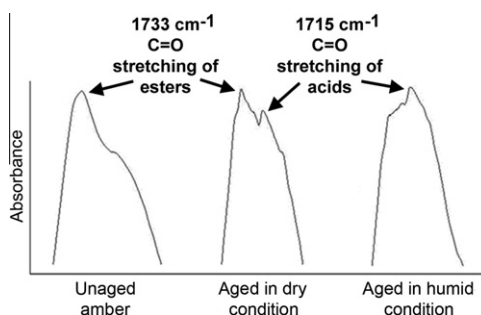
Hydrolysis of Baltic amber during thermal ageing – An infrared spectroscopic approach

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HIGHLIGHTS

- ▶ Hydrolysis as a degradation mechanism during ageing of Baltic amber is investigated.
- ▶ A survey on ATR–FTIR spectra of unaged and thermally aged amber samples is carried out.
- ▶ Absorbance intensities of carbonyl groups at different frequencies are analysed.
- ▶ Production of acids is observed mainly on samples aged in a humid environment.
- ▶ Hydrolytic reactions during degradation of Baltic amber are confirmed.

GRAPHICAL ABSTRACT



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ABSTRACT

To enable conservation of amber in museums, understanding of chemical changes is crucial. While oxidation has been investigated particularly well for this natural polymer, further degradation phenomena in relation to humidity and pollutants are poorly studied or still unknown. Attenuated total reflectance–Fourier transform infrared spectroscopy was explored with regard to Baltic amber. A systematic spectroscopic survey of a wide range of thermally aged model amber samples, exposed to different microclimatic conditions, showed significant changes in their spectra. Samples aged in a humid and acidic environment or exposed to a humid and alkaline atmosphere generally exhibited a higher absorbance intensity of carbonyl groups at frequencies assigned to acids than unaged samples, samples aged in drier conditions and samples immersed in an alkaline solution. Baltic amber comprises succinate ester, which may be hydrolysed into communol and succinic acid. The survey thus provided evidence about the progress of hydrolytic reactions during degradation of Baltic amber. Infrared spectroscopy was shown to have significant potential for providing qualitative and quantitative chemical information on hydrolysis of amber, which will be of interest for the development of preventive conservation techniques for museum collections of amber objects.

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Introduction

Chemical characterisation of museum amber objects is essential to understanding the mechanisms by which they degrade and to propose techniques and procedures for their stabilisation. The degradation pathways involving thermal oxidation [1–4] and photo-oxidation [5] have been investigated in detail for Baltic amber or

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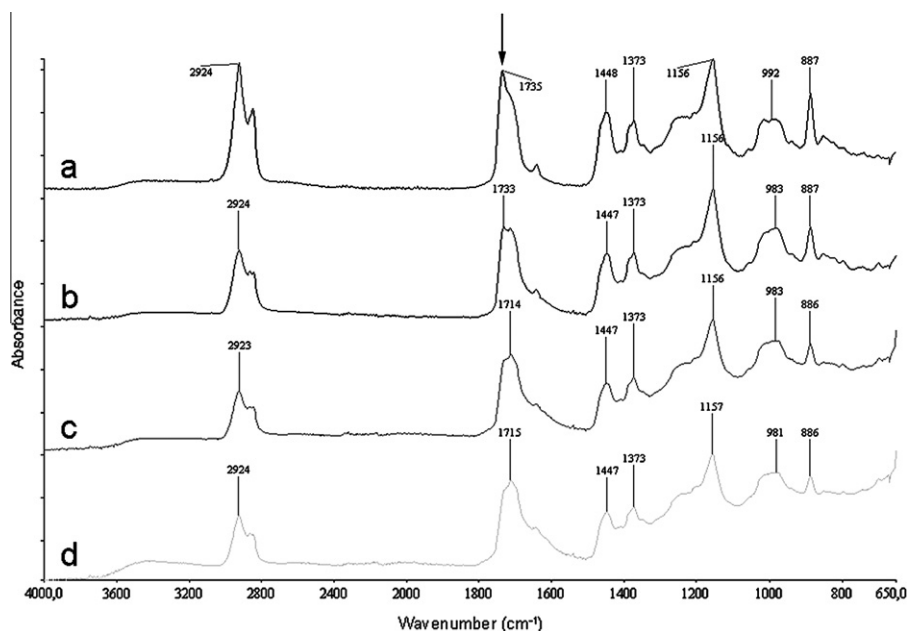


Fig. 1. Example of splitting and following shift of the absorbance peak (indicated by the arrow) assigned to C=O groups of esters and acids from $1733 \pm 2 \text{ cm}^{-1}$ to $1715 \pm 1 \text{ cm}^{-1}$, in Baltic amber exposed to a humid atmosphere (100% RH) during thermal ageing at $70 \pm 2 \text{ }^\circ\text{C}$ (a – before ageing, b – after 11 days, c – after 23 days, d – after 35 days).

Table 1

Microclimates, equivalent real life conditions they represent and accelerated thermal ageing setups for amber samples.

Microclimate	Equivalent real life condition	Accelerated thermal ageing setup
Sample exposed to oven atmosphere, $\leq 20\%$ RH	Object exposed to open air	Open containers
Sample exposed to internal atmosphere, $\leq 20\%$ RH	Object stored in dry case	5 g of silica gel placed inside closed containers
Sample exposed to internal anoxic atmosphere, $\leq 20\%$ RH	Object buried in arid soil	5 g of silica gel and an oxygen absorber ^a placed inside closed containers
Sample immersed in liquid, 100% RH, pH ≤ 5.5	Waterlogged object	20 mL of deionised water placed inside closed containers
Sample exposed to internal atmosphere, 100% RH	Object stored in humid case	13 mL of deionised water placed inside closed containers
Sample immersed in liquid, 100% RH, pH 3	Object buried in highly acidic bog	20 mL of buffer pH 3 ^b placed inside closed containers
Sample exposed to internal highly acidic atmosphere, 100% RH	Object stored in humid case in presence of highly acidic pollutants	13 mL of buffer pH 3 ^b placed inside closed containers
Sample immersed in liquid, 100% RH, pH 5	Object buried in acidic bog	20 mL of buffer pH 5 ^c placed inside closed containers
Sample exposed to internal acidic atmosphere, 100% RH	Object stored in humid case in presence of acidic pollutants	13 mL of buffer pH 5 ^c placed inside closed containers
Sample immersed in liquid, 100% RH, pH 10	Object buried in alkaline bog	20 mL of buffer pH 10 ^d placed inside closed containers
Sample exposed to internal alkaline atmosphere, 100% RH	Object stored in humid case in presence of alkaline pollutants	13 mL of buffer pH 10 ^d placed inside closed containers

RH – relative humidity.

^a Ageless Z from Conservation by Design (Bedford, UK).

^b Commercial solution of citric acid, NaOH and HCl from Merck.

^c Commercial solution of citric acid and NaOH from Merck.

^d Commercial solution of boric acid, KCl and NaOH from Merck.

Succinite. However, further degradation phenomena initiated or accelerated by water vapour and pollutants are poorly studied. While documentation for oxidation of Baltic amber is available, the possibility of hydrolysis as a degradation pathway has not been established. That is the purpose of the present publication.

For identification and chemical characterisation of amber, the most widely used analytical technique is Fourier transform infrared (FTIR) spectroscopy [6–8], providing information on composition and degradation processes in a micro-destructive way. In particular, attenuated total reflectance (ATR)–FTIR has been shown to be useful for quantification [1,2,5] and also localisation [4] of oxidation in Baltic amber. In previous related studies [1,2], through the analysis of ATR–FTIR spectra of unaged and thermally aged Baltic amber samples, one spectroscopic feature drew the attention

Table 2

Acidity values of chemical compounds relevant to indoor museum environments and experimental conditions.

Compound	Molecular formula	Acidity (pK_a) at $25 \text{ }^\circ\text{C}$
Nitrous acid	HNO_2	3.40
Formic acid	CH_2O_2	3.74
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2$	4.76
Citric acid (polyprotic) ^a	$\text{C}_6\text{H}_8\text{O}_7$	$\text{pK}_{a1} = 3.15$ $\text{pK}_{a2} = 4.77$ $\text{pK}_{a3} = 6.40$
Ammonium ion	NH_4^+	9.25
Boric acid	H_3BO_3	9.24

^a pK_{a3} value for citric acid is not relevant, as during this research solutions of citric acid were buffered over the range of pH 3–5.

of the investigators. All carbonyl compounds absorb in the region $1760\text{--}1665\text{ cm}^{-1}$ due to the stretching vibrations of the $\text{C}=\text{O}$ bond. During thermal ageing, the absorbance peak at $1733 \pm 2\text{ cm}^{-1}$, assigned to carbonyl ($\text{C}=\text{O}$) groups of esters and present in all the spectra of unaged samples, showed splitting in two peaks and, in some instances, a following shift to $1715 \pm 1\text{ cm}^{-1}$, which is a frequency attributed to $\text{C}=\text{O}$ groups of carboxylic acids (Fig. 1). This observation suggested the progression of hydrolytic reactions associated with the input of energy as heat and was investigated further. In the current work, a systematic survey of ATR-FTIR spectra of thermally aged Baltic amber in various microclimates [2] is presented, specifically with focus on hydrolysis as a possible degradation mechanism.

Materials and methods

In a previous study [2], artificial thermal ageing at $70 \pm 2\text{ }^\circ\text{C}$, in the absence of light, was used to accelerate the degradation of representative Baltic amber samples in various microclimates relevant to burial, museum storage, use and display conditions (Table 1). Amber powder was produced from a large piece of raw Succinite from Rav Fehrn ApS (Søborg, Denmark). Pellets were obtained from pressed powder and were used as test material because presentation of amber in that format resulted in excellent repeatability and optimal signal to noise ratio in ATR-FTIR spectroscopy. The ATR-FTIR spectra were collected using a Perkin Elmer Spectrum One FTIR spectrometer equipped with an ASI DurasamplIR single

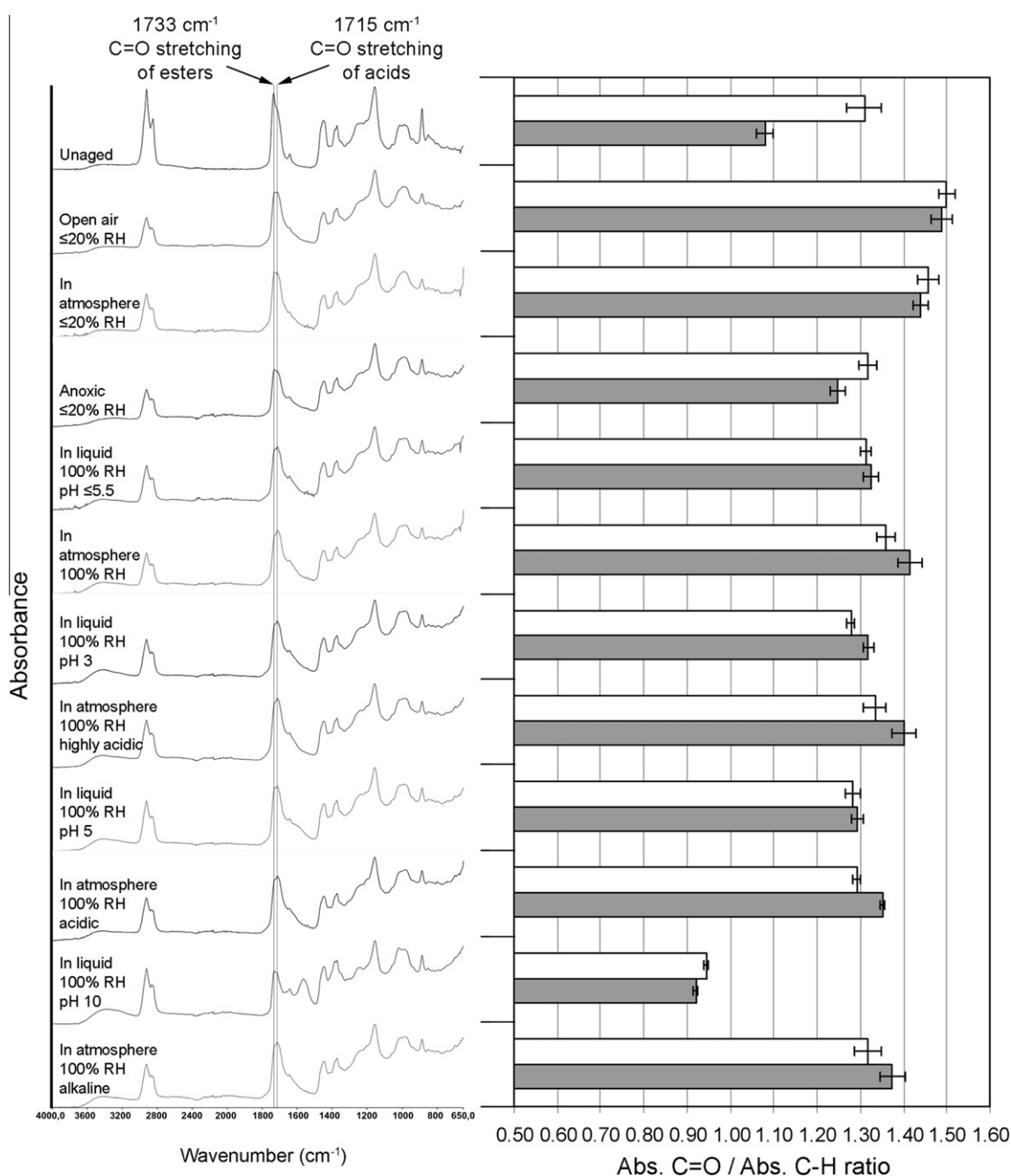


Fig. 2. ATR-FTIR spectra of unaged and thermally aged (after 35 days) Baltic amber samples. Two vertical lines are plotted at 1733 cm^{-1} and 1715 cm^{-1} for easier comparison. Esters and acids carbonyl groups concentrations for each microclimatic condition are showed on the right. Key to the symbols: white bar – average concentration of $\text{C}=\text{O}$ groups of esters, filled bar – average concentration of $\text{C}=\text{O}$ groups of acids (error bars represent standard errors).

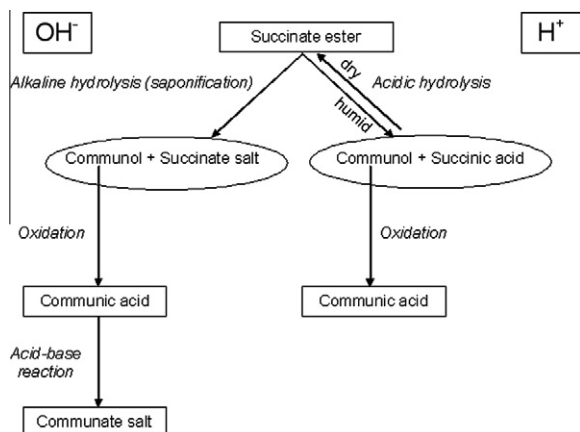


Fig. 3. Degradation pathways of succinate ester in alkaline (OH^-) and acidic (H^+) conditions.

reflection ATR accessory and Perkin Elmer Spectrum software version 6.2.0. Measurements were performed before the ageing process, then after 11, 23 and 35 days of ageing. Materials, instrumentation and procedures used for sample preparation, production of microclimates, thermal ageing and ATR–FTIR analysis are described in greater detail in the above mentioned work [2].

Three additional microclimates (i.e., highly acidic, acidic and alkaline atmospheres, 100% RH) were included in order to investigate their potential effect on the hydrolysis of amber. Buffer solutions comprising citric and boric acids were used to generate acidic and alkaline humid atmospheres. At first sight, selection of such acids appears to have no relevance to museum situations, whereas sulphur dioxide, ozone and various acids (e.g., nitric, nitrous, formic and acetic acids) in the gas phase, and sulphate, nitrate and ammonium in particulate matter are detected in indoor museum environments and are known to cause damage to materials [9,10].

Pilot experiments were carried out using aqueous solutions of acetic acid (33%) and ammonium hydroxide (5%), to obtain acidic and alkaline micro-environments respectively. At temperatures

above ambient and particularly at 70°C the pH values of those solutions were unstable, precluding any investigation into the chemical behaviour of Baltic amber exposed to the microclimatic conditions of interest. The use of buffer solutions was then considered to be the best way to ensure stability of the pH values. Table 2 presents a list of acidity values expressed as dissociation constants at logarithmic scale (pK_a) assigned to a number of compounds [11,12]. The findings suggest that the humid atmospheres created with buffer solutions are as aggressive as real indoor museum humid atmospheres, although different organic acids may have very different effects on some materials.

To assess the hydrolysis of esters into carboxylic acids in the amber samples during accelerated ageing, changes in the shape of the infrared band assigned to $\text{C}=\text{O}$ groups, i.e., splitting of the peak at $1733 \pm 2 \text{ cm}^{-1}$ and, when present, following shift to $1715 \pm 1 \text{ cm}^{-1}$, were investigated on raw absorbance spectra, without manipulations or baseline corrections. A quantitative analysis was also carried out by means of determining and comparing the intensity of peaks, a method previously used in other studies [2,4,5]. Concentrations of $\text{C}=\text{O}$ groups of esters and acids for each microclimatic condition were calculated, based on relative absorbance intensity values at $1733 \pm 2 \text{ cm}^{-1}$ and $1715 \pm 1 \text{ cm}^{-1}$, determined by height, and calibrated against the unchanging band at $1450 \pm 20 \text{ cm}^{-1}$ attributed to $\text{C}-\text{H}$ bonds of $>\text{CH}_2$ and $-\text{CH}_3$ groups. Quantitative measurements were performed on spectra of unaged samples and samples aged for 35 days; three spectra were used for each measurement. Because the peak at $1715 \pm 1 \text{ cm}^{-1}$ is normally overlapped by the one at $1733 \pm 2 \text{ cm}^{-1}$ in spectra of unaged amber, causing the stretching of $\text{C}=\text{O}$ bonds of unreacted acids to be manifested by a shoulder, its height was measured exactly at 1715 cm^{-1} .

To investigate whether hydrolytic reactions in Baltic amber also occur at room temperature, a number of deaccessioned museum archaeological objects, including Neolithic Baltic amber beads found in Skanderborg, Denmark, dated 3000–2000 years BCE, from the National Museum of Denmark, were analysed by ATR–FTIR and the acquired spectra were compared to the ones obtained from the accelerated ageing experiment.

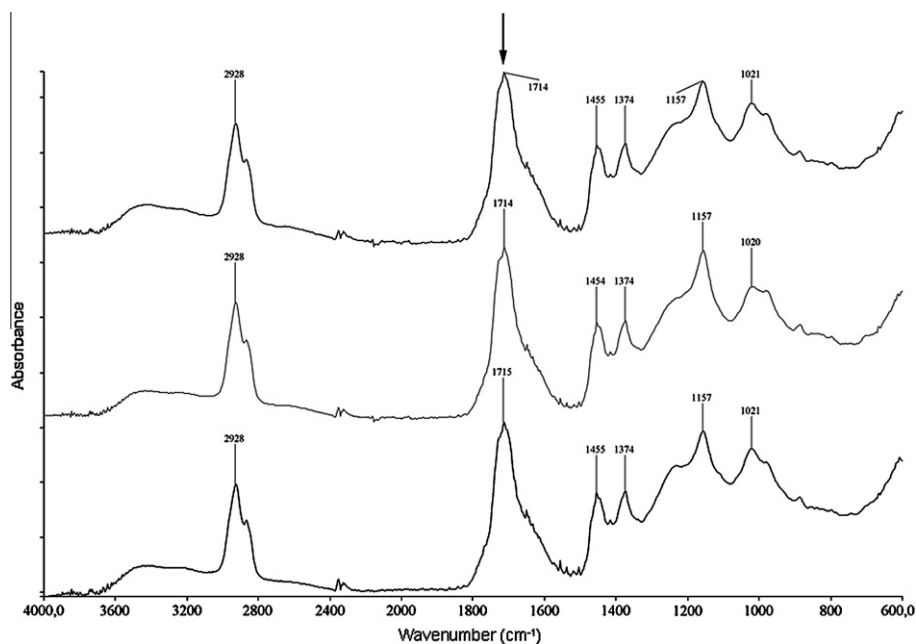


Fig. 4. Representative ATR–FTIR spectra of archaeological Baltic amber objects. The infrared band used to identify hydrolysis of the amber samples is indicated by the arrow.

Results and discussion

Hydrolysis of esters into carboxylic acids was determined using ATR–FTIR spectroscopy by evaluating the changes in the shape of the infrared band assigned to C=O groups, which were observed between $1733 \pm 2 \text{ cm}^{-1}$ and $1715 \pm 1 \text{ cm}^{-1}$.

Fig. 2 presents a stack plot of ATR–FTIR spectra of unaged and thermally aged Baltic amber samples together with esters and acids C=O groups concentrations versus all ageing conditions. Spectroscopic data showed a significant shift of the peak attributed to carbonyl groups of esters towards lower frequencies associated with carboxylic acids, whenever amber samples were aged in a humid (100% RH) and acidic microclimate. The same trend was also observed in samples exposed to a humid and alkaline atmosphere. On the other hand, samples that were exposed to a drier atmosphere ($\leq 20\%$ RH), where the amount of moisture available for hydrolytic processes was lower, or immersed in an alkaline solution, where hydrolysis likely took place as saponification without acids formation, only showed a splitting of the original peak with a predominance of ester groups. In short, there was strong evidence of hydrolytic reactions taking place in most of the humid microclimates, produced by presence of water or buffer solutions, during ageing.

The chemical composition of Baltic amber is well known [13,14]. The characteristic ester is succinate ester, which could be hydrolysed into communol and succinic acid (i.e., two other typical components of Baltic amber) in humid and acidic conditions. Additional oxidative reactions [2,4] may cause the production of communol acid from communol. Such oxidative reactions were limited in samples that were immersed in liquid, where the concentration of oxygen was lower than in air, and could not occur in samples that were exposed to an anoxic atmosphere.

In humid and alkaline conditions the main ester in Baltic amber, succinate ester, had an opportunity to undergo hydrolysis to form communol and a succinate salt. Also in this case, further oxidative reactions may cause the production of communol acid from communol, explaining the splitting of the carbonyl peak in samples that were immersed in the alkaline buffer and the shift of the same peak in samples that were exposed to an alkaline atmosphere. When the samples are immersed in buffer pH 10 solution, diterpenic salts, namely communates, are generated by the reaction between communol acid and the alkaline solution [2]. The formation of saline by-products was confirmed by the presence of a new infrared band around 1550 cm^{-1} in the ATR–FTIR spectra related to the samples aged in the alkaline buffer. The described reactions are summarised in Fig. 3.

Regarding the ATR–FTIR analyses of archaeological Baltic amber objects, in all the instances spectroscopic data exhibited a higher absorbance intensity of C=O groups at the frequency assigned to acids (Fig. 4), thus confirming the significance of hydrolysis as a degradation process also at room temperature.

The results of this study demonstrated that hydrolysis of esters in Baltic amber is a significant degradation mechanism, establishing a new important finding for this type of material. Hydrolytic reactions were identified from their products, showing that the

infrared spectra of thermally aged samples in a humid environment were characterised by a shift of the peak attributed to carbonyl groups of esters towards lower frequencies assigned to acids. The ATR–FTIR spectroscopy was used to conduct a qualitative survey to identify hydrolysis of amber samples during accelerated ageing. In addition, it is proposed that the application of this technique has a significant potential for quantitative investigations. Hence, it would be of interest to further characterise degradation of Baltic amber attributed to hydrolytic processes, presenting a kinetic follow up of the reactions during ageing, in future studies.

Amber degradation is related to both low and high RH levels. Low levels cause surface cracking, increasing opacity [15], and acidic vapours off-gassing [3], while the rate of hydrolysis may be hastened by moisture, as suggested by this investigation. An RH value in the intermediate region between $37 \pm 2\%$ RH and $53 \pm 2\%$ RH, suitable also for storage and exhibition of other organic heritage materials [16], should be appropriate. It is also important that the RH remains stable, to avoid structural damages due to shrinking and swelling oscillations [15]. Thus, the ideal conditions to preserve Baltic amber museum objects should include both pH and humidity control, for instance using pollution scavengers and humidity stabilisers regularly replaced inside storage, transport and display cases.

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References

- [1] Y. Shashoua, M.L. Degn Berthelsen, O.F. Nielsen, *J. Raman Spectrosc.* 37 (2005) 1221–1227.
- [2] G. Pastorelli, *J. Cult. Herit.* 12 (2010) 164–168.
- [3] G. Pastorelli, J. Glastrup, *Anal. Bioanal. Chem.* 399 (2011) 1347–1353.
- [4] G. Pastorelli, J. Richter, Y. Shashoua, *Spectrochim. Acta A* 89 (2012) 268–269.
- [5] G. Pastorelli, J. Richter, Y. Shashoua, *Polym. Degrad. Stab.* 96 (2011) 1996–2001.
- [6] C.W. Beck, E. Wilbur, S. Meret, D. Kossove, K. Kermani, *Archaeometry* 8 (1965) 96–109.
- [7] J.H. Langenheim, C.W. Beck, *Sci., New Ser.* 3679 (149) (1965) 52–55.
- [8] M. Guiliano, L. Asia, G. Onoratini, G. Mille, *Spectrochim. Acta A* 67 (2007) 1407–1411.
- [9] F. De Santis, V. Di Palo, I. Allegrini, *Sci. Total Environ.* 3 (127) (1992) 211–223.
- [10] M. Ryhl-Svendsen, J. Glastrup, *Atmos. Environ.* 36 (2002) 3909–3916.
- [11] D. Shriver, P. Atkins, *Inorganic Chemistry*, University Press, Oxford, 1999.
- [12] E.P. Serjeant, B. Dempsey, *Ionization Constants of Organic Acids in Aqueous Solution*, IUPAC Chemical Data Series 23, Pergamon Press, Oxford, 1979.
- [13] J.S. Mills, R. White, L. Gough, *Chem. Geol.* 47 (1984) 14–39.
- [14] K.B. Anderson, in: K.B. Anderson, J.C. Crelling (Eds.), *Amber, Resinite, and Fossil Resins*, American Chemical Society, Washington, 1996, pp. 105–129.
- [15] R.S. Williams, J.B. Waddington, J. Fenn, *The society for the preservation of natural history collections, Collection Forum* 2 (6) (1990) 65–75.
- [16] M.F. Mecklenburg, C.S. Tumosa, A. Pride, *ASHRAE J.* 46 (6) (2004) S18–S23.