

Thermal investigations of amber and copal

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Abstract

Stimulated by the “Amber ISBC” in Gdansk/Poland, 15 amber samples (Baltic area, Germany, Africa, Meso- and South America) and 3 copal samples (Africa, Meso- and South America) were investigated by thermal analysis (DTA, TG, DTG, combined with mass spectrometry) as well as pyrolysis-gas chromatography. IR false colour thermography was added to study the burning behaviour of the samples. Characteristic compounds like abietic acid, succinic acid, several terpenes or sesquiterpenes and related compounds were detected for amber and copal and compared in the sense of fingerprinting. One sample of incense was included in the investigations because amber was used as a kind of incense along the Baltic Coast through many centuries.

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1. Introduction

The 14th conference of the International Society for Biological Calorimetry (ISBC) took place in Gdansk/Poland, the amber capital of the world, for which reason this conference was named the “Amber ISBC”. This title stimulated some investigations of the thermal behaviour of this interesting material, its history and background. Only few true thermal analyses are found in the literature, e.g. [1–6], more by IR spectroscopy [3,5,7–12] and more by pyrolysis-gas chromatography, mass spectrometry and nuclear magnetic resonance [5,11,12–17]. Some of these investigations were aimed at establishing scientific methods for determining the age and geographic origin of amber samples. These questions become more and more important since false amber pieces appear on the market in increasing amounts. Such ambers are produced from ground amber scraps or even synthetic resins, often with interesting inclusions of (recent!) plants and small animals. On the other hand, the data obtained allow establishing cladograms of kinship for various ambers and finding relationships between them and their origins. Copal as a rather young resin and incense as a freshly harvested one were incorporated into the present amber investigations because of their various common similarities, properties and applications.

The name “amber” is not a strict scientific name for a special kind of resin, but indicates a group of very heterogeneous resins with quite different chemical and physical properties. Ragazzi et al. [4] use the name *sensu lato* for fossil resins in general, and so do other scientists. Nevertheless, amber may be described as a natural resin with an approximate composition of 75% C, 10% H, 15% O and up to 0.4% S. Amber consists of a polyester of resin acids with a high percentage of abietic acid (C₂₀H₃₀O₂) and only 3–8% succinic acid, rendering a global formula of C₁₀H₁₆O for amber in general [18,19]. Its melting point varies between 290 and 384 °C [20], sometimes told 360–410 °C [18]. The botanical origin of amber is still being discussed.

The age of amber spans several hundred million years, from the tertiary period into the carbon (30–360 million years). The worldwide largest deposit of amber (“succinit”) along the Baltic coast dates from 30 to 50 million years. Copal which is often confused with “true” amber and sold in many countries under the wrong name is much younger than amber with ages between several hundreds and many thousands of years [21]. Its pyrolysis/gas chromatography shows that mainly cyclic and polycyclic carbohydrates and a few aromates are present in copal (unpublished results). The most recent resin in the investigations was Indian incense, a product of the incense tree *Boswellia serrata* that is still collected in larger amounts in the Arabic world (from different *Boswellia* bushes) and exported everywhere [18]. Two hundred and fifty organic compounds were identified in incense, in parts identical with those found in amber and copal. In

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medieval times, simple amber pieces were used along the Baltic coast instead of the expensive beeswax to illuminate houses, giving birth to the German name “Bernstein” = “Brennstein” (burning stone) that is used in many Scandinavian countries also. Moreover, amber was used in the North to odourise and disinfect rooms like incense around the Mediterranean Sea.

The present paper concentrates on thermal investigations in a broader sense for a variety of amber and copal samples of different origins. Own investigations oriented on some recent papers that tried to obtain a classification of amber by thermal analysis [4] and observed a close correlation between the age of a sample and the appearance of the main exothermal peak in DTG curves [4], that informed about screening techniques (including thermography) on early Eocene ambers from a rich lagerstätte in North Italy [6,22], and about comparable thermogravimetric studies of Kauri copals from New Zealand aging between recent, 30 thousand and 40 million years [23]. These references together with those mentioned above helped to interpret the own results of corresponding amber and copal samples.

2. Experimental

2.1. Amber, copal and incense samples

Samples of amber and copal were collected during traveling, obtained as friendly gift from a collection at the Gdansk University or bought together with incense in several Berlin mineral shops. Amber originated in a large part from the Baltic coast (eight samples), including one sample found at palaeolithic excavations and an uncounted number of small pieces in all colours and degrees of turbidity and translucency. One sample was autoclaved before use. Further specimens of the same Baltic type originated from different soils in Berlin, a very rich deposit near Leipzig/Germany and the bank of the river Elbe/Germany. As a counterpart from Mesoamerica, amber from the Dominican Republic was included also.

Copal specimens came from Colombia, the Dominican Republic, the Amber Bay in Madagascar and an unknown place in East Africa. Two of these samples showed inclusions of small insects. The Indian incense was a commercial product (Primavera Life, Sulzberg, Germany) such as sold in esoteric shops around the world.

2.2. Thermal analysis

Thermal analysis of amber and copal was hampered by the fact that their volatile products condensed in cooler capillary parts of the apparatus and blocked them after a short experimental period. Therefore, only a few samples were analysed in the way which is described in an earlier paper of the present authors in more detail [24]. Briefly, a simultaneous thermal analysis apparatus (STA 409 C, Netzsch, Selb/Germany) was coupled via a Skimmer[®] system to a mass spectrometer (BALZERS QMG 421, Balzers Liechtenstein). This combination rendered the conventional thermoanalytical curves (T, DTA, TG, DTG) and additionally the ionic currents (IC) in the multiple ion detection (MID) mode. Mass numbers could be followed up to 300

m/z; attributions to molecular fragments were made according to ref. [25]. The samples to be measured have been obtained by milling a powder from the solid amber particles utilizing a dentist's drill. By visual inspection it was possible to distinguish between “pure” amber and dark inclusions of small insects. The obtained powders differed remarkably in colour.

2.3. Collection of headspace volatiles, gas chromatography, mass spectrometry

Amber, copal and incense samples were heated on fumigating charcoal tablets ($\varnothing = 4$ cm; Primavera Life, Sulzberg, Germany; temperature above 320 °C). An inverted funnel was placed a few centimetres above the tablet and connected by Teflon tubes via a 100 mg charcoal filter-tube (ORBO, Supelco Inc.) to a micropump (DC6V, FürGut, Tannheim, Germany) sucking at a constant air flow of 100 ml min⁻¹ (flowmeter 8443A/1, Baily, Fischer & Porter, Göttingen, Germany). Collecting times amounted to 20 min. The filter was eluted with 300 μ l dichlormethane containing 50 ng μ l⁻¹ dodecane as an internal standard. 1 μ l samples were analysed with coupled gas chromatography–mass spectrometry (GS–MS) (Fisons GC model 8060; Fisons MD 800 quadrupole MS) using a J&W 30 m DB5–ms capillary column 0.32 mm internal diameter and 0.25 μ m film thickness. The temperature rose from 40 up to 280 °C with a rate of 10 K min⁻¹. Mass fragments from 35 to 400 *m/z* were detected after an effluent ionisation of 70 eV. Resulting spectra were compared with library spectra [26].

2.4. Infrared thermography

Glowing and burning samples of amber and copal were investigated by an IR camera using the near infrared between 3.5 and 5 μ m (Inframetrics SC 1000, FLIR Systems, Germany). Its characteristic data are: focal-plane array of 256 \times 256 detector elements (Pt-Si-Schottky diodes); microcooling device of the stirling type; autospan and span mode; output tif-files; evaluation of the thermograms in Adobe PhotoShop 7.0 with the eye-dropper tool and the Navigator Info to compare colours in the thermograms and in the corresponding temperature scales. For more details see ref. [27].

3. Results and discussions

3.1. Characteristics of amber, copal and incense

The sizes of the different samples varied between a few hundred milligrams and many grams, their colour changed from a very light lemon yellow to intensive dark brown, for clear specimens as well as for translucent or turbid ones. The surface was mainly smooth from polishing, but sometimes also barked by weathering. Some samples were rather brittle and broke into very small pieces when handled; others were robust and had to be sawed to get the correct milligram amounts for the experiments. The smell after rubbing was always pleasant but varying considerably from piece to piece.

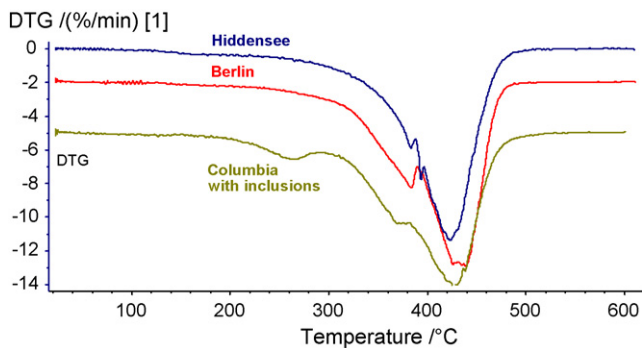


Fig. 1. Differential thermogravimetric (DTG) curves of three amber samples originating from the island Hiddensee (Baltic Sea, Germany) (top), Berlin (Germany) (centre), and Colombia (bottom). (In nitrogen; heating rate 10 K/min; the y-axis shows the percentage mass loss per minute.)

All samples that entered the investigations were “natural” amber, i.e. stones without any wet or dry thermal treatment as often applied to change the colour, eliminate the turbidity or to get inclusions of air looking like botanical flakes (squamae) or parts of leaves. Only polishing was allowed for removing the bark layer on the surface. “True amber” or “pressed amber” (ambroid) produced from amber scraps by high pressure were also excluded.

3.2. Thermal analysis

Quite unexpectedly, the DTA curves were rather unspecific for all kinds of amber investigated. The curves were less-structured and exhibited weak phenomena reflecting only general features of the thermal characteristics (e.g. endothermal tendency for evaporation processes and exothermal signal groups for decomposition reactions which partially overlap). This behaviour, on the other hand, is not that untypical for such a kind of multi-component natural product as amber. Only the first time derivatives (DTG) of the thermogravimetric (TG) curves allow for deducing some differences which in fact represent small partial steps being more or less distinctly expressed in the form of additional DTG effects. However, it is difficult to

deduce reliable chemical or calorimetric conclusion from these differences.

For a first illustration of amber thermograms, Fig. 1 shows the DTG curves of two Baltic ambers (Hiddensee and Berlin) and a Colombian one with insect inclusions. The first two slopes are rather similar with a double peak around 390 °C for the Hiddensee and a single peak for the Berlin sample. The South American one differs considerably with a shift of the mentioned peak to 383 °C and a pronounced TG step around 260 °C. The maximum decomposition rate for the main TG step is reached for all three samples between 410 and 420 °C. Similar slopes are shown in ref. [23] with more strongly structured curves for the recent samples and a significant shift of the main peak to higher temperatures. Colombian amber had a main peak at 400 °C with a few secondary peaks on the left flank as observed and discussed in ref. [4] also.

More details concerning the Hiddensee amber as a representative sample are given in Fig. 2. It includes the conventional set of three thermoanalytical (TA) curves, i.e. (i) the percentage mass loss in the thermogravimetric (TG) curve together with (ii) its first time derivative (DTG, cf. Fig. 1), and (iii) the temperature difference (DTA) curve. Furthermore, the simultaneously recorded ionic current (IC) curves for the relative mass numbers $m/z = 18, 43$ and 44 (in the following named m18, m43, and m44, respectively) are presented.

As mentioned above, the DTA curve under nitrogen is not specific. A weak deviation from the base line in the endothermal range starts at about 380 °C; it might be attributed to evaporation processes forming the so-called fire gases. When the decomposition process accelerates, a predominance of exothermal reactions causes the broad signal around 420 °C. The total mass loss of amber at about 500 °C amounts to 96.1% indicating low ash content in this sample.

The nearly complete decomposition proceeds in one main step up to about 500 °C which is in good agreement with some literature data (e.g. [5]), while ref. [4] shows TG curves that drop to zero between 560 and 600 °C. All main components of amber reported in the literature can be detected via the mass numbers being characteristic for a whole group of substances,

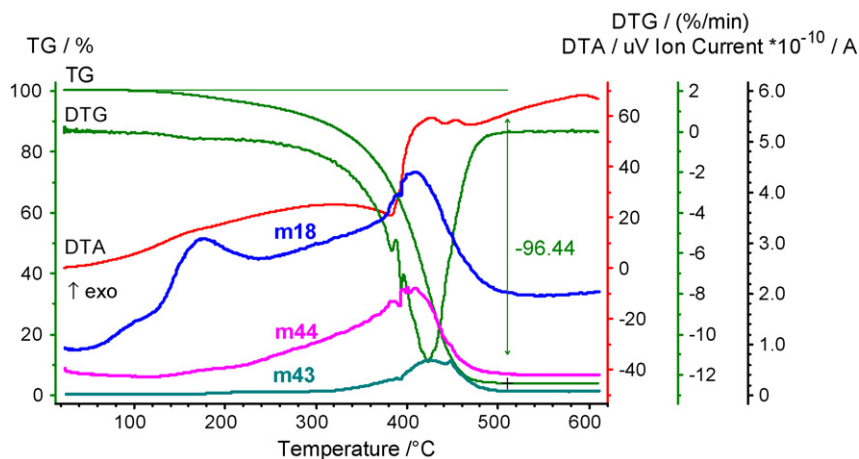


Fig. 2. Conventional thermoanalytical (TA) curves (TG, DTG, DTA) together with the ionic current (IC) curves for the mass numbers m18 (H_2O^+), m43 (C_3H_7^+) indicating the isopropyl fragment, and m44 (CO_2^+) for the dark brown and turbid Hiddensee amber of Fig. 1.

e.g. carbonic acids, terpenoides, sesquiterpenoides, naphthalene derivates, abietic acid, etc. Their fragments appear in this broad peak between 300 and 460 °C.

The IC curve for m18 (H_2O^+) demonstrates that, obviously, two kinds of water liberation occur: a slight mass loss of ca. 3% between 140 and 250 °C and a second one together with all decomposition products. The first water release could be interpreted in terms of “free” water with liberation at somewhat higher release temperatures. The second water peak, on the other hand, clearly has to be regarded as reaction water the amount of which (cf. the peak area) is not considerably greater than the first one. Anyway, condensation reactions based on alcohols, phosphates as well as redox reactions of the heteroatom-containing hydrocarbons have to be taken into account.

The mass number m43 (C_3H_7^+) indicates iso-propylic fragments from sesquiterpenoides, m44 (CO_2^+) carbon dioxide from the decarboxylation of different acids. Probably, one of these acids should be abietic acid, which is reported in the literature to be an essential constituent of amber. The characteristic mass numbers m91 (C_7H_7^+ for alkylated aromates) and m105 ($\text{C}_7\text{H}_5\text{O}^+$ for benzoyl compounds) can be detected with remarkable intensity (not shown here for the Hiddensee amber, but cf. Fig. 3). Other fragments connected with amber are detected via m128 ($\text{C}_{10}\text{H}_8^+$; naphthalene, M^+), m132 ($\text{C}_{10}\text{H}_{12}^+$; tetraline, M^+) and m159 which are typical for sesquiterpenoids without iso-propylic groups. Finally, the m34 (H_2S^+) peak between 340 and 430 °C indicates sulphur that is common in amber with low concentrations between 0.1 and 0.4% [20]. A rather similar overall thermoanalytical impression is obtained with a sample found in Berlin, also belonging to the Baltic family. Its characteristics: a total mass loss of 99.50%, a less pronounced water peak (m18) around 150 °C, the two peaks of abietic acid (m91, m105) and a sharp naphthalene peak (m128) (data not shown).

These results shall be compared with those of a specimen of quite different origin: a light honey-coloured, transparent amber from the Dominican Republic (Fig. 3). The DTA trace is as unspecific as before; only a weak exothermal effect can be observed at about 383 °C without any further interpretation.

There is a slight difference in the exothermal shift in the high-temperature range.

The TG curve, however, is remarkably differing as two main steps can be clearly observed. The IC curves for the fragments m91 and m105, indicating abietic acid [5], reveal that the main products of amber decomposition are released in both partial steps. The same has been observed for the mass numbers m128, m132, m159 all being characteristic for sesquiterpenoids, naphthalene, etc. (not shown).

As before, the maximum decomposition rate is reached around 420 °C; the total mass loss of 96.9% indicates the same ash content. It is noteworthy that the water release and the release of decomposition products exhibit a qualitatively different curve shape—the processes do not seem to be related to each other. Furthermore, low intensity, but evident peaks were detected for m198, m200 and m202—they represent substituted sesquiterpenoids in amber as their qualitative curve shape is the same as for the m43 fragment of isopropyl groups from sesquiterpenoids.

A possible explanation for the partition of the TG curve into several steps might be the lower age of the Mesoamerican amber (20 million years). Due to a smaller degree of cross-linkage in the polymer network, a fraction of higher-volatile polymers may be contained in younger amber which then would be expressed in an additional low-temperature TG step. In total, one can conclude that Figs. 2 and 3 confirm that Baltic and Dominican amber belong to different amber classes.

3.3. Pyrolysis-gas chromatography

Fifteen samples of amber and three of copal were included in the investigations; moreover, one of incense just for comparison. All samples were burnt on glowing charcoal tablets as used for distribution of essential oils from natural resins. The smell of the smoking or burning amber is very specific and typical, so that a well-trained tester from the perfume industry might be able to distinguish the specimens and determine the origin just with his nose. The following three figures depict chromatograms comparing the (i) three classes of resins, (ii) amber as well as (iii) copal samples of different origin. Evaluating the chromatograms

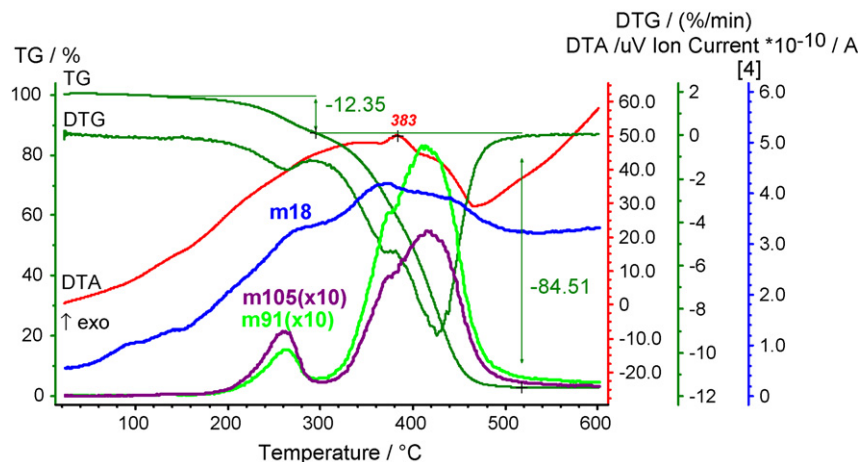


Fig. 3. TA and IC curves for water (m18) and two typical fragments of abietic acid (m91, m105) for light honey-coloured, transparent amber from the Dominican Republic. “(×10)” Indicates that this ion current was amplified 10-fold compared with m18 and the axis at the right.

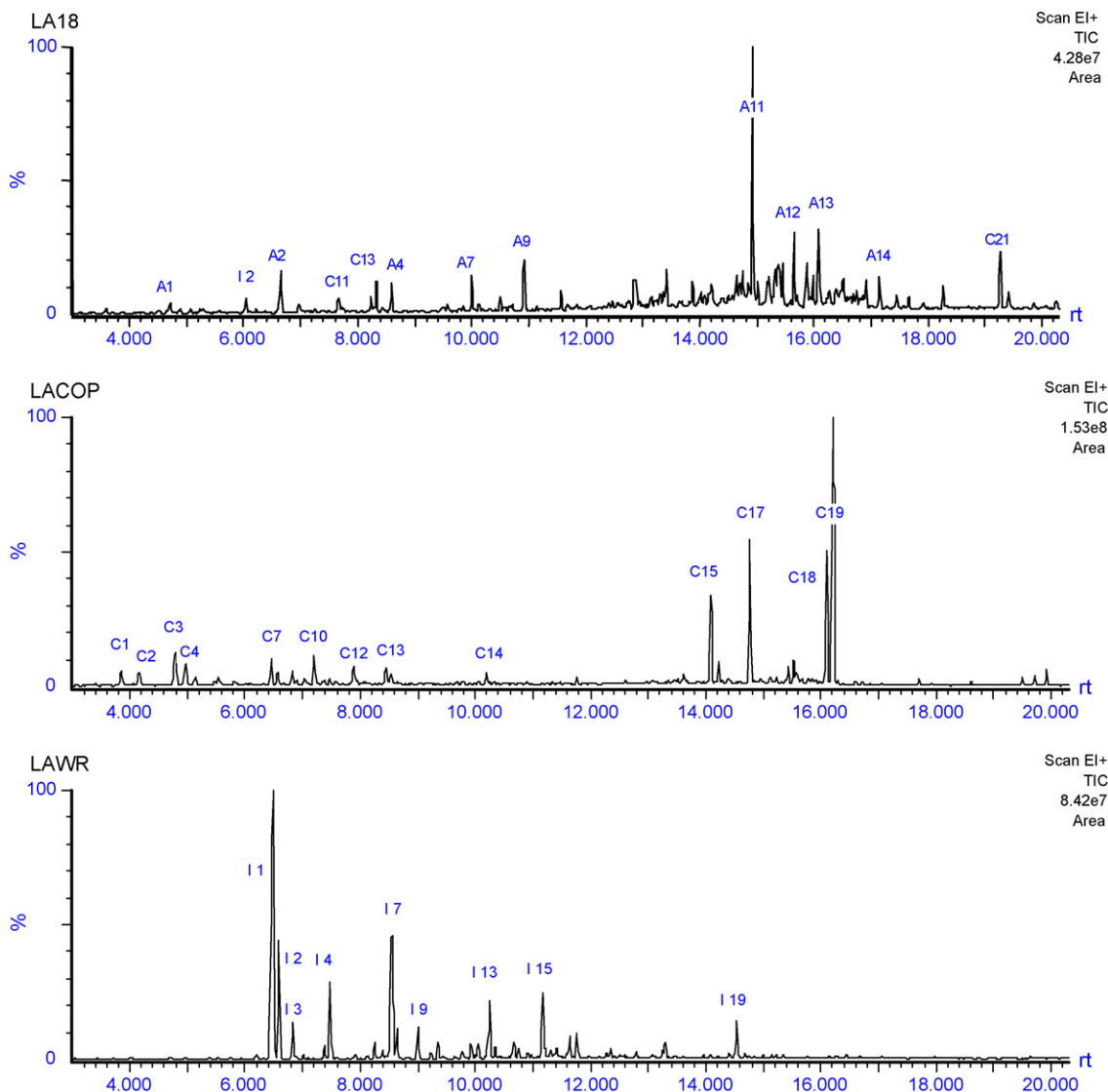


Fig. 4. Comparative gas chromatograms from pyrolytic investigations of Baltic amber (top), Colombian copal (centre) and Indian incense. Retention times are given in minutes, peaks in relative heights. The numbers indicate typical peaks for A, amber; C, copal; and I, incense. IntStd: internal standard (see Fig. 5).

it should be kept in mind, that they are scaled to the largest peak as 100% and that their absolute values can be obtained as ratio to the (constant) internal standard in each of the chromatograms.

Fig. 4 compares typical chromatograms of amber, copal and incense with one another. Already at the first glance, the incense spectrum deviates completely from the two others with peaks concentrating at lower retention times (=rt). There are two prominent early terpene peaks: I1 for α -pinene and I2 for carene, respectively, I5 indicates β -pinene as a further terpene; I7 stands for isopropyl toluene (cymene) that is also present in all other amber and copal samples (named A4, C13 there). Further incense compounds seen in the chromatogram are thujol (I9), β -thujon (I13), thujenol acetate (I15) and bourbone (I19). In contrast to incense, the most prominent peaks for amber and copal are concentrated in the second half of their chromatograms, where there are no more peaks for the incense.

Fig. 5 shows chromatograms of two Baltic type ambers from the island of Hiddensee (top) and Berlin (centre) and for Domini-

can Republic amber (bottom). Peaks that are also found in copal are indicated by their C numbers. The chromatograms differ considerably and give the impression that “fingerprinting” of amber should be possible with this method. As mentioned above, the isopropyl toluene peak (A4 at $rt = 8.46 \pm 0.13$ min; $n = 15$ samples) is present in all three runs, although not very distinct; moreover two further peaks of unidentified origin, peaks A11 (14.91 ± 0.02 min) and A14 (17.14 ± 0.02 min). Most prominent besides A11 are A9 for borneole, A8 for camphor, and C14 for trimethyl hydroxymethyl cycloheptene in the brown Hiddensee sample, that are small in the two other specimens.

The Berlin amber is dominated by the peak of the internal standard at $rt = 11.52$ min, the peak C15 (13.85 min) for damascone, and C19 (15.97 min) for aromadendrene. Identified compounds are shown by C1 (dimethyl cyclohexane), C3 (tetramethyl cyclopentene), A1 (*p*-dimethyl benzene), C5 (dimethylene cyclohexane), C12 (mesitylen), C13 (isopropyl toluene), and C15 (damascone), for example.

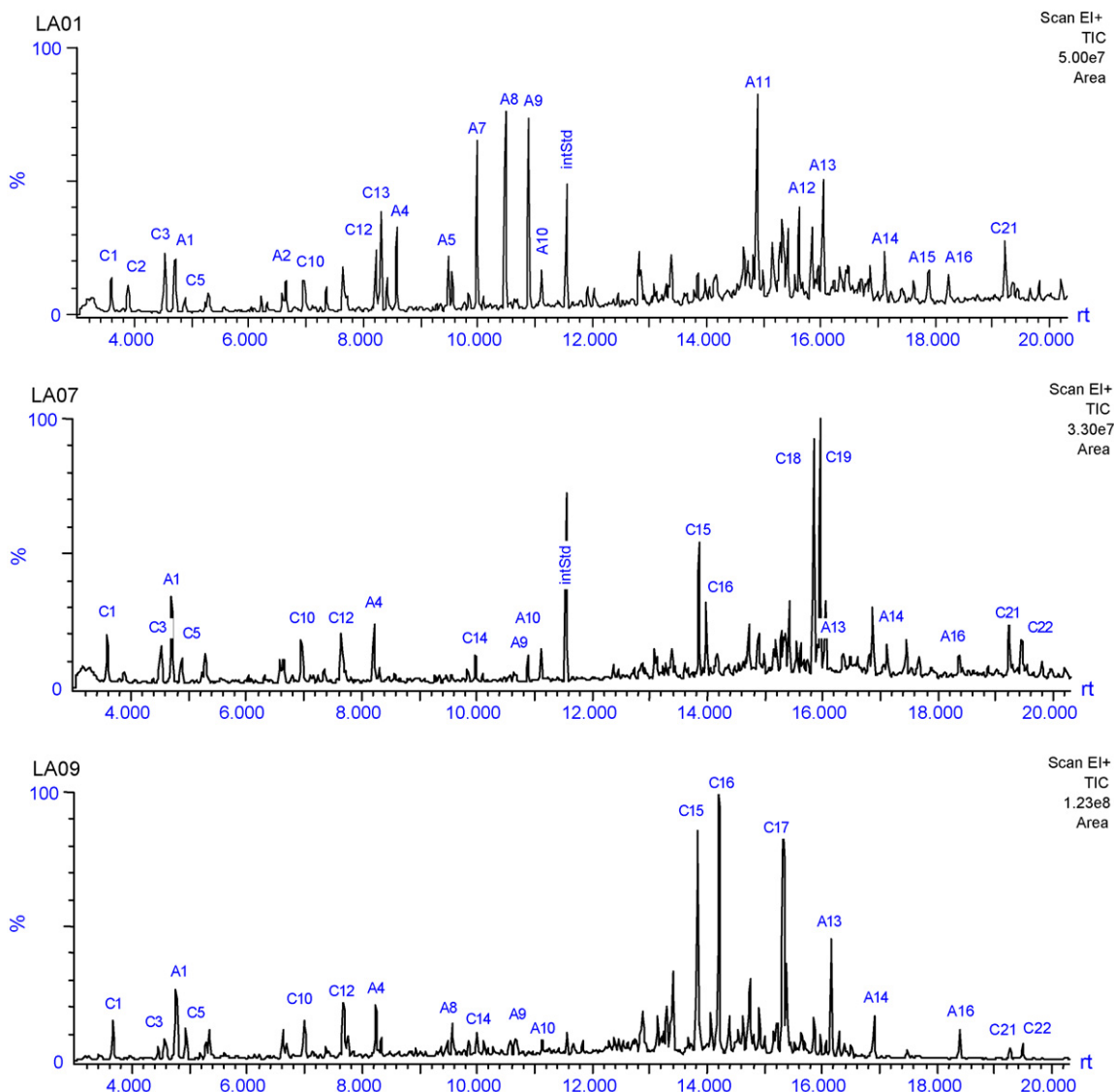


Fig. 5. Comparative gas chromatograms of amber: brown Baltic amber from the island Hiddensee (top), honey-coloured, transparent Baltic amber from Berlin (centre), and light honey-coloured, transparent amber from the Dominican Republic (bottom). Further details as in Fig. 4.

The third amber sample, a light yellow piece from the Dominican Republic, is similar to the Berlin sample at early retention times with the same peaks in the same relative height as above. The later peaks C15 and C16 are the largest followed by a new peak C17 (α -gurjunen) and by the same peaks as in the Berlin sample at the upper end. The altered heights in the latter two spectra give the impression of two quite distinct amber families in the sense of fingerprinting (see above).

An attempt was made to find out whether three characteristic amber peaks A4, A11 and A14 are connected with one another and have constant ratios of their peak areas for all samples. Calculations showed that the standard deviations of these ratios for A4 and A11 compared with A14 amounted to about 60%, that of A11 with A4 to even 160%. This indicates that they are in no direct relation to one another. A11 is the highest peak in two-thirds of the 15 amber samples and small in only 2 cases. Its relative peak areas vary considerably from 0.23 to 34.03% with a mean of $7.6 \pm 8.6\%$ (of the calibration sample). Auto-

claved Baltic amber even had a relative area of 121.8% (data not shown).

Finally, the chromatograms of three copals are shown in Fig. 6: from the Colombian Pacific coast (yellow-brown), from the Dominican Republic (light yellow) and from East Africa (transparent, pale yellow). All three have their prominent peaks between 13.0 and 16.5 min retention time with two additional peaks (C21 and C22) of unknown origin at the upper end, specially pronounced in the African sample. The lower end of the spectrum is similar to that of the ambers with C4 (*p*-dimethyl benzene) instead of A1 (ethyl benzene).

3.4. Infrared thermography

The burning behaviour of amber and copal was investigated by IR false colour thermography [27]. Glowing charcoal tablets were placed in a bowl with sand to distribute the heat more evenly. The samples were lit with a match when they started to

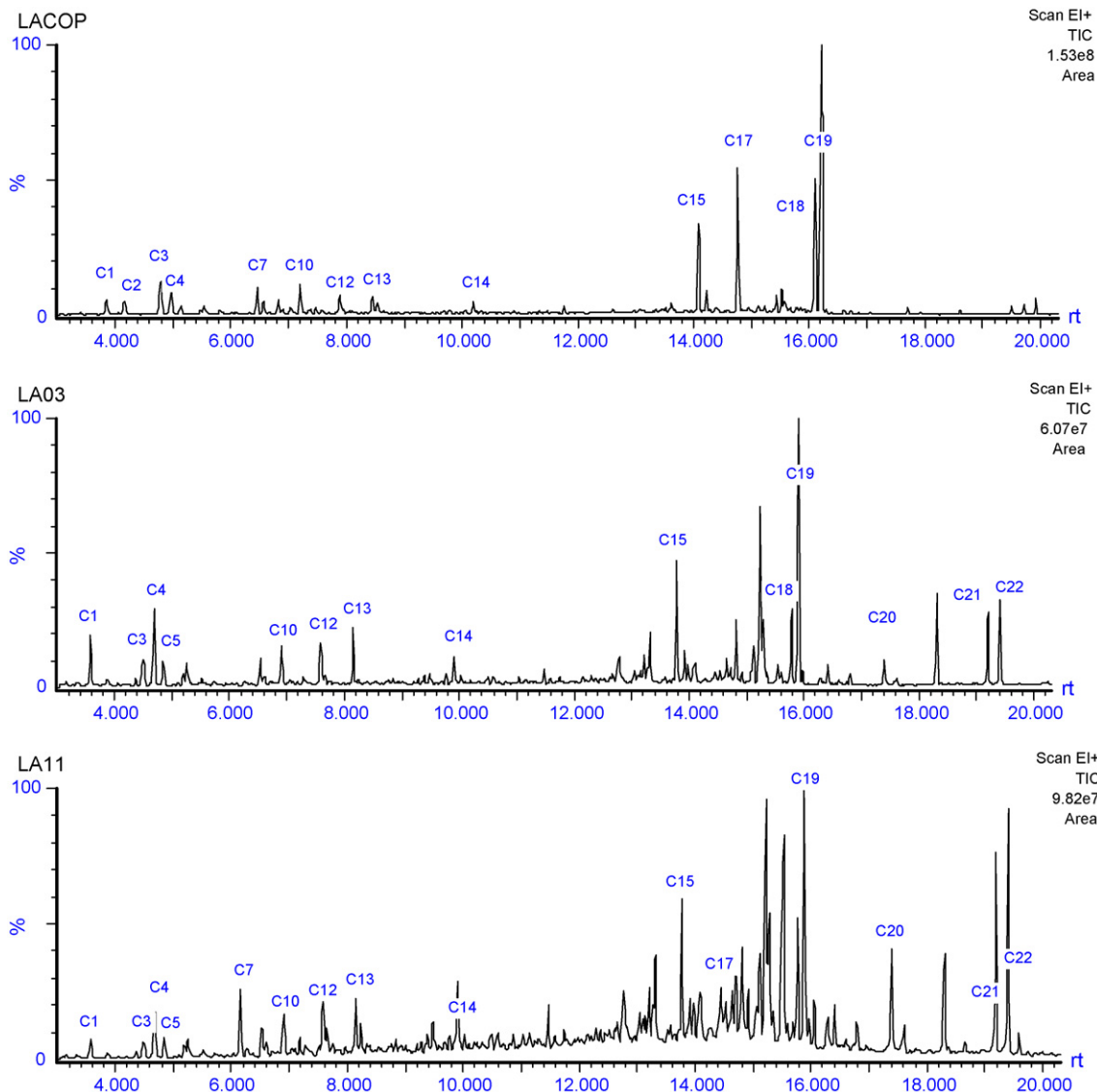


Fig. 6. Comparative gas chromatograms of copal samples: light yellow Colombian copal (top), honey-coloured, turbid Dominican Republic copal (centre), and lemon yellow, turbid East African copal (bottom). Further details as in Fig. 4.

melt. They burned with a bright yellow to white flame with a strong flag of black soot. Burning was in all cases connected with a very intensive and pleasant smell of coniferous material. This smell was so strong that it was not possible to investigate burning in small rooms, but only in a large hall of a research institute or outside in an open place.

Fig. 7 shows an IR thermogram of burning Baltic amber. The charcoal temperature was above 450°C , the upper limit of the camera, while the brightest parts of the flame were about 430°C with frames at 280°C and lower. The black soot at the upper end of the flame was at about 100°C as observed at other camera settings. Because of the rather quick burning on charcoal a second kind of experiment could be more similar to the way amber was used as light source in former days and even now in the Dominican Republic. The sample was squeezed in a vertical wooden stick, slit in the upper end, and lit directly without prior heating. Amber and copal easily started to burn with a calm flame of less soot formation than before (Fig. 8).

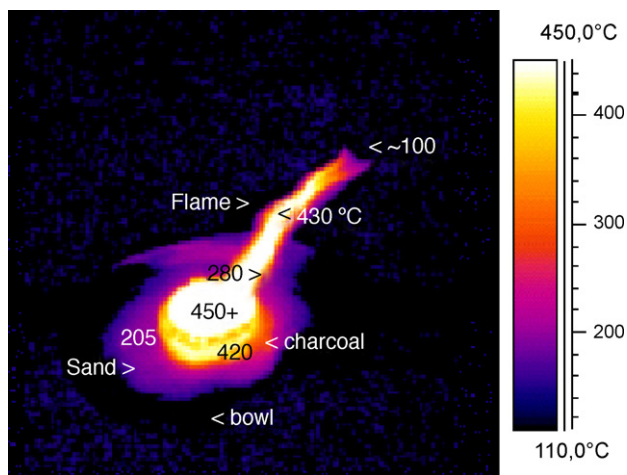


Fig. 7. IR thermography of a burning piece of amber placed on a glowing charcoal tablet. “450+” means temperatures above 450°C out of the range of the camera. Photo M. Röllig, Berlin.

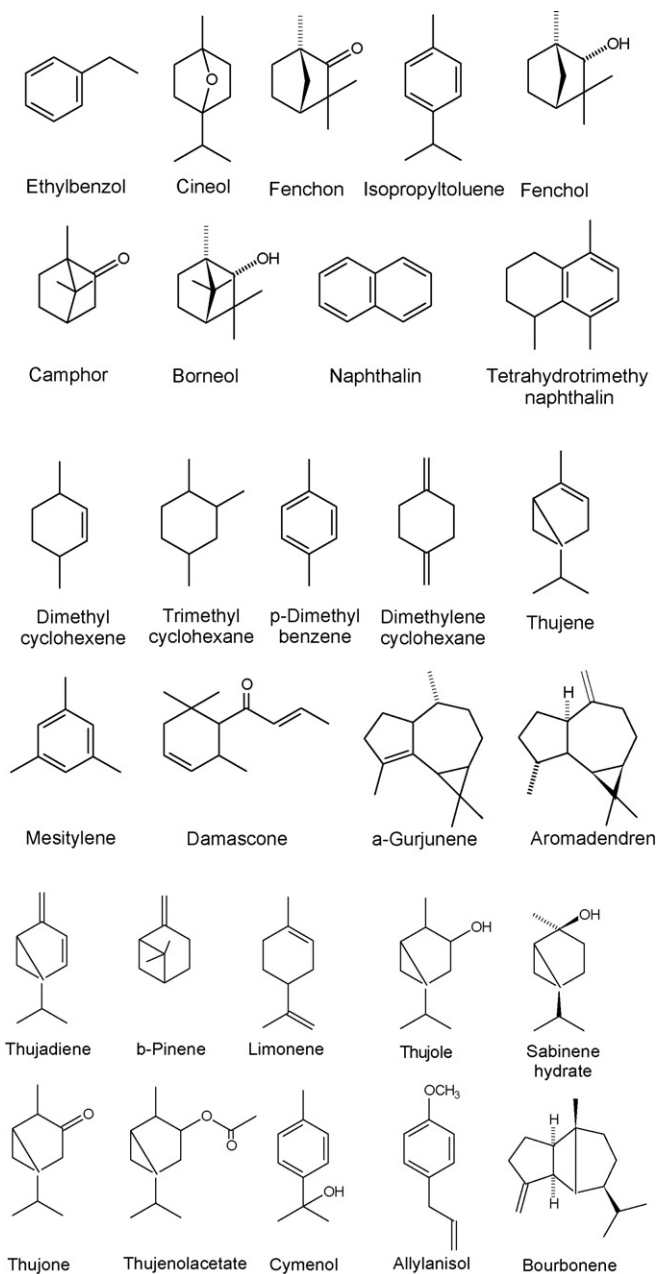


Fig. 8. Structural formulae of essential compounds in amber (top), copal (centre) and incense (bottom) [26].

4. Conclusion

Amber and copal are by themselves fascinating objects and also from the scientific point of view. As highly complex natural polymers they provide information about their composition, their origin and their age. Infrared spectrometry seems to be the easiest and most promising approach for fingerprinting, but pyrolysis-gas chromatography also produces descriptive results. Thermal analysis in form of differential scanning calorimetry as well as thermogravimetry alone [4] or coupled with mass spectrometry guarantee new insights into processes that occur when samples are heated up and give information about age, maturity,

origin and thermal history of fossil resins. All three methods have the advantage that minimal amounts of samples are needed for significant results.

A pleasant coincidence happened just a few days before the Amber ISBC started in Gdansk. On the 31st of May 2006, 3 days before the opening, exciting news came in the radio and was printed in newspapers. On the Forum Romanum of Rome a 3000-year-old grave was opened that contained the skeleton of a 30-year-old woman. As sign of her noble origin or position she wore a necklace of—amber [28, see also 29].

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