The analysis of archeological amber and amber from the Baltic Sea by thin-layer chromatography

The appearance of amber objects which have been found in graves in Slovenia, dating from the 4th and the 5th century B.C. is very similar, both in colour and fragility. When these products are compared with amber from the Baltic Sea it can be seen that the two substances are not similar. An analysis is therefore necessary to solve the question of identity and after trying several methods we found thin-layer chromatography to be the most convenient. Radioactive carbon dating[1] and neutron activation analysis[2] have proved to be very useful in archeology for determining the age of many objects, but for the study of the cultural material of historic and prehistoric periods chemical analysis can also be used[3–5]. Thin-layer techniques have been recently much used for the identification of resins and therefore this method was used in our investigation.

Materials and methods

Different samples of Baltic amber were used for the analysis. It is known that amber can be found in different forms varying from completely transparent light yellow pieces, through different shades of yellow to dark yellow, and is sometimes completely opaque. Reddish-brown samples can also be found. All the above mentioned forms of amber were analysed and divided into three groups. In the first group only light yellow, transparent pieces were used. The second group contained dark yellow, non-transparent pieces and the third group contained reddish-brown, usually opaque pieces.

On examining the archeological samples we found that they do not differ in appearance. They all have a reddish-brown colour, with crystalline cleavage, and therefore they are semitransparent and brittle.

The specific gravity was determined for all three groups of Baltic amber as well as for the archeological samples.

For thin-layer chromatography all samples were powdered. The impurities which could be present in the form of calcium carbonate and earth were removed by shaking the powder with diluted hydrochloric acid and subsequently washing with distilled water, at first in the beaker and then on filter paper. The samples were dried *in vacuo* over calcium chloride.

Solubility of the purified samples was determined in various organic solvents. 2 ml of the solvent was added to 0.2 g of sample, the mixture was then shaken for 3–4 h at 40° and finally left to stand overnight at 20°. The clear solution was pipetted into a weighing bottle. The solvent was evaporated and the dry residue was weighed. The following solvents were tested: methanol, ethanol, acetone, chloroform, ethyl acetate, amyl acetate, turpentine, and benzene.

Silica Gel G coated glass plates were used for thin-layer chromatography. A solvent system consisting of 95 parts of benzene and 5 parts of methanol (v/v) was used[6]. All chromatograms were allowed to run in the same solvent system once and then again (double development).

The spots were located either by inspection of the chromatogram under U.V. light or by spraying it with antimony trichloride reagent[6].

Results and discussion

Measurement of the specific gravity showed differences among the three groups of Baltic amber. The specific gravity of the yellow pieces was 1.0360–1.0643, and 1.1159 for the reddish-brown specimens. No significant differences among archeological samples were observed in so far as they did not contain inclusions of non-resinous material. The specific gravity of archeological amber was 1.1544.

A significant difference in the solubilities of the two types of amber was observed and the results are shown in Table I. It can be seen that Baltic amber is less soluble than archeological samples in all the solvents tested except in turpentine oil, where an inverse phenomenon occurred. In the first six solvents tested the archeological amber was 3–6 times more soluble than Baltic amber. The solutions of archeological amber were an intense yellow colour while the solutions of Baltic amber varied from light yellow to almost colourless.

TABLE I

SOLUBILITY OF ARCHEOLOGICAL AND BALTIC AMBER IN VARIOUS ORGANIC SOLVENTS

Solvent	*Solubility (g dry residue per 100 ml solvent)*	
	Archeological sample	*Baltic sample*
Methanol	3.5	0.7
Ethanol	4.9	1.2
Ethyl acetate	4.1	1.2
Amyl acetate	5.4	1.4
Acetone	6.2	1.1
Chloroform	4.0	1.3
Turpentine	1.0	1.4
Benzene	0.8	0.3

Results of the thin-layer chromatography are shown in Figs. 1 and 2. Chromatograms with single development are shown in Fig. 1; the spots were made visible with antimony trichloride. Great differences can be observed among chromatographed amber samples dissolved in ethanol (1), chloroform (2), acetone (4), and ethyl acetate (5). Fig. 2 shows twice developed chromatograms of both types of amber samples dissolved in ethyl acetate and acetone. The difference in the number of spots is evident. While the ethyl acetate solution of archeological amber only separated into two or three spots, seven to eight spots were observed on the chromatogram of Baltic amber. The difference is even more pronounced if the acetone–amber solutions are compared after double development.

In addition to the differences in appearance and fragility there are also great differences in the measured properties between the two samples. The dissimilarity of the two types of amber is already evident from the differences in specific gravity. The different solubilities of the two resins in various solvents further support this idea and this is also reflected in qualitative chromatographic analysis. The number of spots clearly indicates that the resins do not both contain the same components and that their composition is completely different.

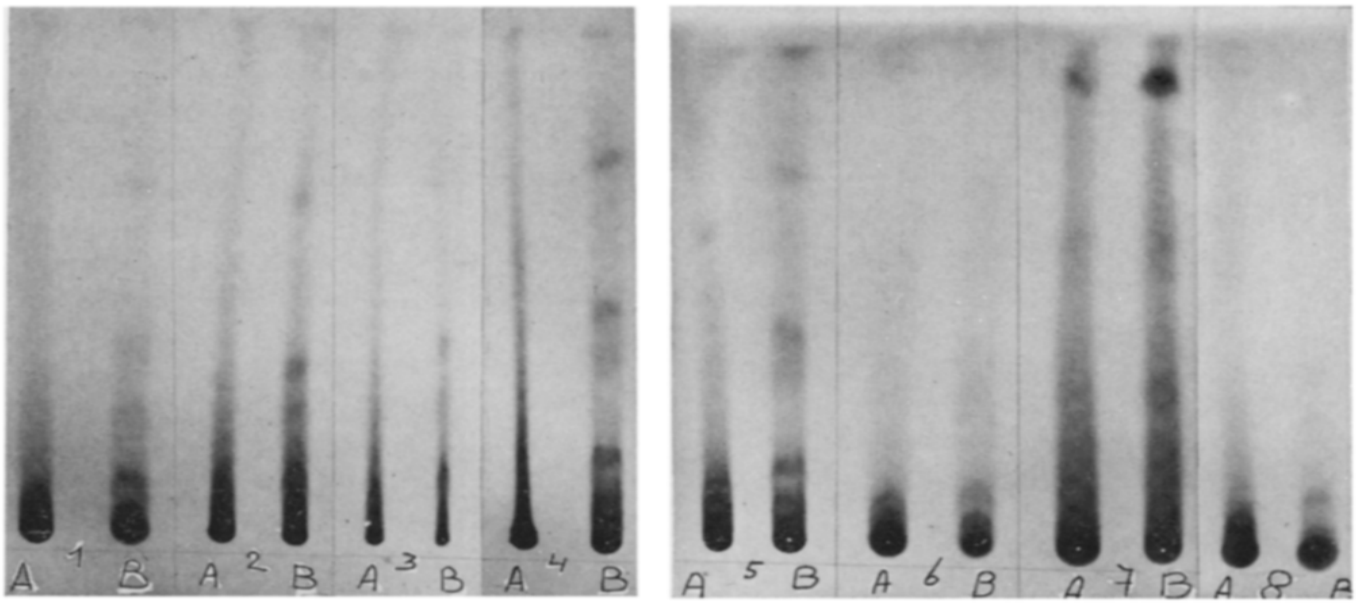

Fig. 1. Thin-layer chromatogram of archeological (A) and Baltic (B) amber dissolved in solvents as described in the text and developed with a benzene–methanol (95:5) solvent system.

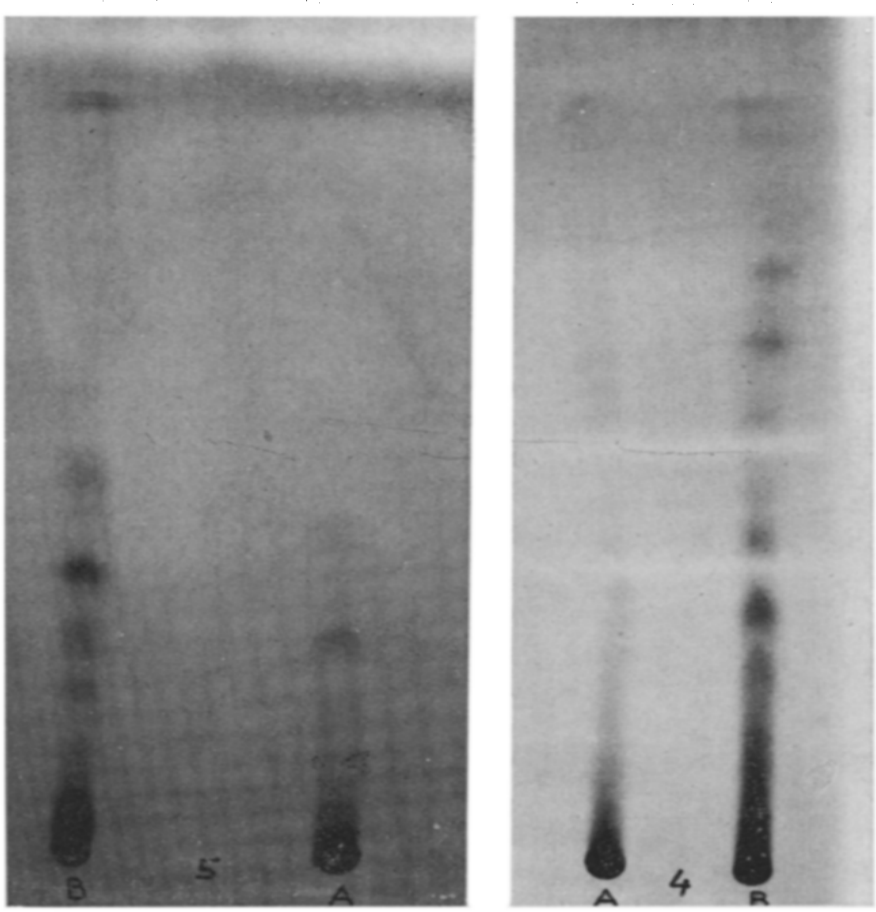

Fig. 2. Thin-layer chromatogram of archeological (A) and Baltic (B) samples of amber dissolved in ethyl acetate and acetone, rechromatographed in the same solvent system.

From our analysis it is evident that none of numerous samples of archeological amber examined showed properties similar to the samples of Baltic amber. Therefore we can conclude that the archeological samples do not originate from Baltic amber but in all probability from a tree resin which was produced similarly to present-day colophony.

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