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Application of FT-Raman and FT-IR in the characterization of archaeological ambers from Romanian collections

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BACKGROUND AND OBJECTIVES OF THE RESEARCH

Rumanite (romanian amber) is found in rare deposits in Buzau county (Romania) and is known to have been exploited since prehistoric times. Because of the historical context, romanian territory being situated near the Baltic amber trade routes, connecting the Baltic area with Southern Europe, the archaeological question that arises is "what is the geological origin of archaeological amber artifacts from romanian collections, Rumanite or Baltic?".

EXPERIMENTAL

Present work tries to answer the archaeological question by using the Raman spectroscopy, already proved as an useful tool in the quest for non-destructive fast methods which could be used to track the geological origins of archaeological ambers [H.G.M. Edwards et al., 1996; R.H. Brody et al., 2001; W. Winkler et al., 2001; J. Jehlicka et. al., 2004]. FT-IR spectroscopy was used complementary on controlled origin amber samples as a well established and practical technique for the structural characterisation and discrimination between amber types [C.W. Beck, 1986; I. Angelini et al., 2005; E.D. Teodor et al., 2009] (figure 1).

Amber Samples (controlled origin and archaeological)

Amber samples of controlled origin (Baltic and Rumanite) were made available from deposits [E.D. Teodor et al., 2009], and archaeological samples from well dated contexts, were provided by Romanian National History Museum (MNIR).

Instrumentation

Bruker Vertex 70 class FT-IR spectrometer equipped with a fiber optic mobile RAMPROBE attached to RAM II module (LN2 Ge detector). FT-Raman spectra were recorded between 50 and 3500 cm^{-1} using Nd:YAG laser (1064 nm, 1-500 mW). Spectral acquisition was made with 100 scans at a 4 cm^{-1} resolution, in situ.
All FT-IR spectra were collected on a Bruker Tensor 27 and analysed at a 4 cm^{-1} spectral resolution.

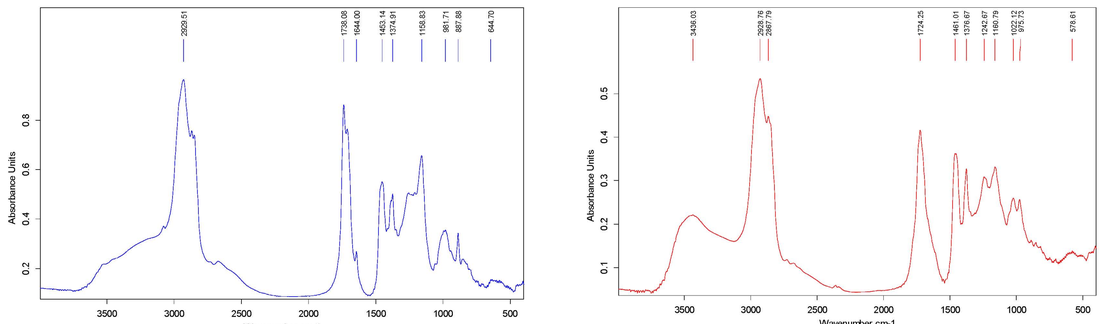


Figure 1. FT-IR spectra of Baltic amber (left) and Rumanite (right). Note: According to Beck, Baltic amber presents a horizontal shoulder at 1250-1160cm-1 followed by a strong signal at 1157 cm-1 [Beck 1986]. Rumanite is characterised by a strong signal at 1241 cm-1 [Angelini 2005]

Table 1. Comparative results between FT-Raman and FT-IR

ID Source	Sample ID	MDA ID	FT-Raman features: ν (C=C)/Rumanite 1608 - 1628 cm^{-1}	FT-Raman features: δ (-CH)/Baltic 1439 - 1445 cm^{-1}	FT-Raman assignment	MDA FT-Raman: PCA FT-Raman assignment	MDA FT-Raman: Cluster FT-Raman assignment	FT-IR features: Baltic shoulder 1250-1160cm^{-1}	FT-IR features: Rumanite signal 1241 cm^{-1}	FT-IR assignment
Baltic	P802	R3	-	+	B	B	B	-	+	B
	P824	B1	-	+?	B?	B	B	+	-	B
	P825	B2	-	+	B	B	B	+	-	B
	P826	B3	+	-	R	B	B	+	-	B
	P828	B4	-	+	B	?	R	+	-	B
	P829	B5	-	+?	B?	?	B	+	-	B
	P830	B6	-	+	B	B	B	+	-	B
	P831	B7	-	+	B	B	B	+	-	B
	P832	B8	-	+	B	B	B	+	-	B
	P833	B9	-	+?	B?	B	B	+	-	B
	P834	B10	-	+	B	B	B	+	-	B
	P835	B11	-	+	B	B	B	+	-	B
	P836	B12	-	+	B	B	B	+	-	B
	P837	B13	-	+	B	B	B	+	-	B
	P838	B14	-	+	B	B	B	+	-	B
	P839	B15	-	+	B	B	B	+	-	B
	P840	B16	-	+	B	B	B	+	-	B
	P841	B17	-	+	B	B	B	+	-	B
Rumanite	P801	R2	+	-	R	R	R	-	+	R
	P801-2	R1	+	-	R	R	R	-	+	R
	P803	R4	?+	-	R?	R	R	-	+	R
	P804	R5	+	-	R	R	R	-	+	R
	P805	R6	+	-	R	R	R	-	+	R
	P806	R7	+	-	R	R	R	-	+	R
	P807	R8	+	-	R	R	R	-	+	R
	P808	R9	?+	-	R?	R	R	-	+	R
	P809	R10	+	-	R	R	R	-	+	R
	P811	R11	+	-	R	R	R	-	+	R
	P812	R12	+	-	R	R	R	-	+	R
	P813	R13	?+	-	R?	R	R	-	+	R
	P815	R14	-	+	B	R	R	-	+	R
	P816	R15	+	-	R	R	R	-	+	R
	P818	R16	+	-	R	R	R	-	+	R
	P820	R17	+	-	R	R	R	-	+	R
	P821	R18	+	-	R	R	R	-	+	R
	P822	R19	+	-	R	R	R	-	+	R
	P823	R20	+	-	R	R	R	-	+	R
UN-Cioclovina	P445	U1	+	-	R	R	R			
	P446	U2	+?	-	R?	R	R			
	P447	U3	+	-	R	R	R			
	P448	U4	+	-	R	R	R			
	P451	U6	+	-	R	R	R			
	P452	U7	+	-	R	R	R			
	P453	U8	+?	-	R?	R	R			
	P455	U9	+	-	R	R	R			
	P457	U11	+?	-	R?	R	R			
	P458	U12	+	-	R	R	R			
	P459	U13	+	-	R	R	R			
	P460	U14	+?	-	R?	R	R			
	P463	U16	+	-	R	R	R			
	P464	U17	+	-	R	R	R			
	P471	U19	+	-	R	R	R			
	P472	U20	+	-	R	R	R			
	P473	U21	+?	-	R?	R	R			
	P474	U22	+	-	R	R	R			
	P475	U23	+	-	R	R	R			
	P479	U25	+	-	R	R	R			
	P482	U27	+?	-	R?	R	R			
	P484	U28	+	-	R	R	R			
	P485	U29	+	-	R	R	R			
	P487	U30	+	-	R	R	R			
	P490	U33	+	-	R	R	R			
	P491	U34	+	-	R	R	R			
	P492	U35	+	-	R	R	R			
	P493	U36	+	-	R	R	R			
	P497	U37	+	-	R	R	R			
	P499	U38	+	-	R	R	R			
	P500	U39	+	-	R	R	R			
	P501	U40	+	-	R	R	R			
	P502	U41	+	-	R	R	R			
	P503	U42	+	-	R	R	R			
	P506	U43	+	-	R	R	R			
	P507	U44	+	-	R	R	R			
	P508	U45	+	-	R	R	R			
	P509	U46	+	-	R	R	R			
	P512	U48	+?	-	R?	R	R			
	P514	U49	+	-	R	R	R			
	P515	U50	+	-	R	R	R			
	P516	U51	+	-	R	R	R			
	P517	U52	+	-	R	R	R			
	P518	U53	+	-	R	R	R			
	P519	U54	+	-	R	R	R			
	P520	U55	+	-	R	R	R			
	P523	U57	+	-	R	R	R			
	P524	U58	+	-	R	R	R			
	P525	U59	+?	-	R?	R	R			
	P528	U61	+	-	R	R	R			
	P529	U62	+?	-	R?	R	R			
	P535	U64	+	-	R	R	R			
	P536	U65	+?	-	R?	R	R			
	P538	U66	+?	-	R?	R	R			
	P539	U67	+	-	R	R	R			
	P542	U68	+?	-	R?	R	R			
	P544	U69	+?	-	R?	R	R			
	P546	U70	+	-	R	R	R			
	P547	U71	+	-	R	R	R			
	P548	U72	+	-	R	R	R			
	P549	U73	+	-	R	R	R			
	P565	U75	-	-	?	R	R			
	P565-2	U74	-	-	?	R	R			
	P567	U76	+?	-	R?	R	R			
UN-Noslac	P220	U77	-	+?	B?	R	R			
	P221	U78	-	-	?	R	R			
	P222	U79	+?	+?	?	R	R			
	P223	U80	+?	-	R?	R	R			
	P225	U81	+	-	R	R	R			
	P227	U82	+	-	R	R	R			
	P230	U83	+	-	R	R	R			
	P232	U84	+?	+?	?	R	R			
	P234	U85	+?	+?	?	R	R			
	P235	U86	+	-	R	R	R			

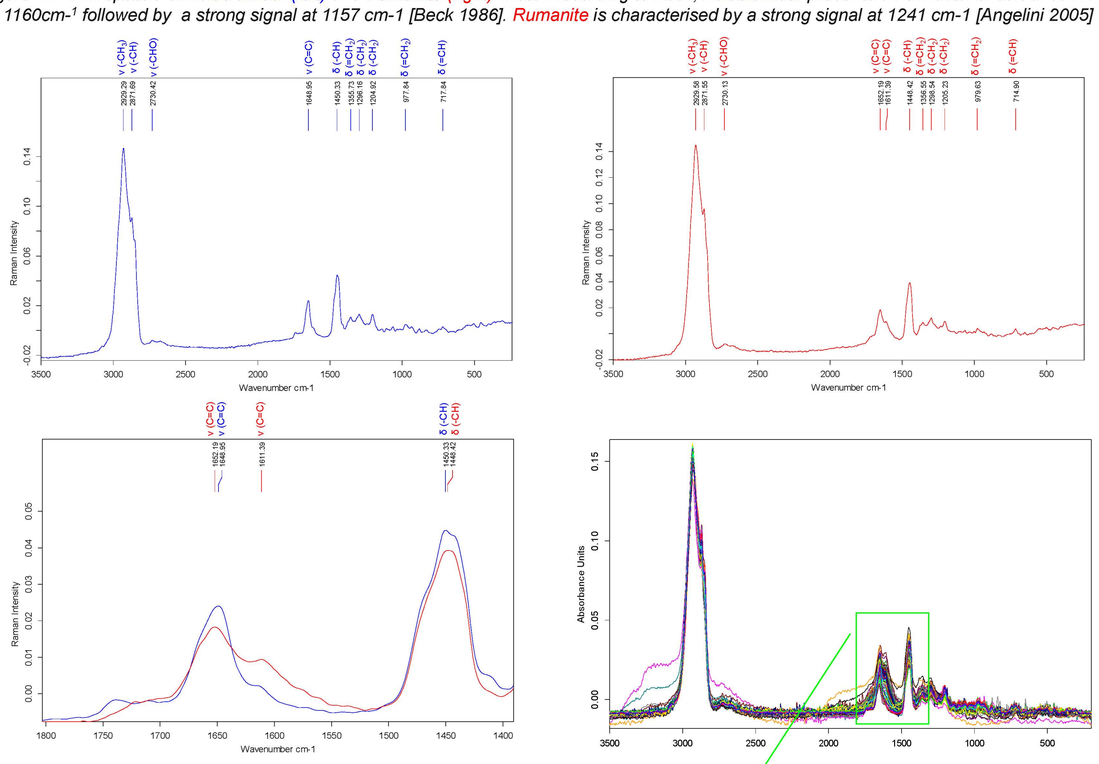
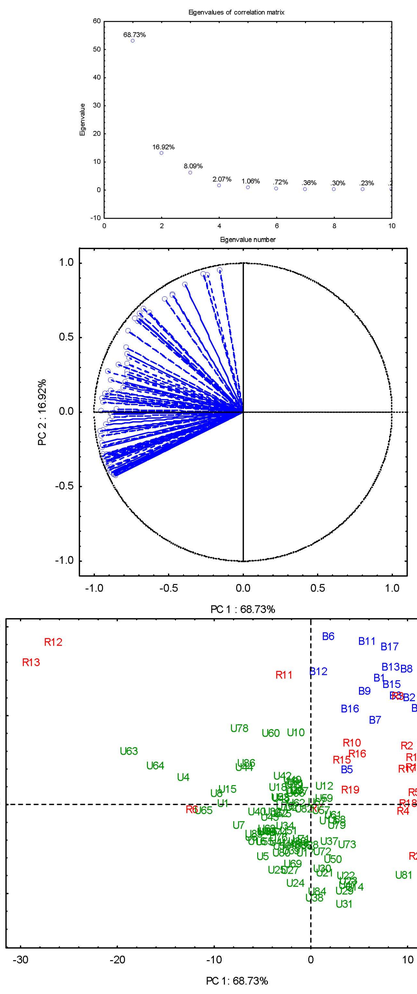


Figure 2. Raman spectra of Baltic amber (top left), Rumanite (top right), comparative detail view of characteristic features for Baltic and Rumanite ambers (bottom left) and test samples from archaeological amber originated from Cioclovina and Noşlac archaeological sites.



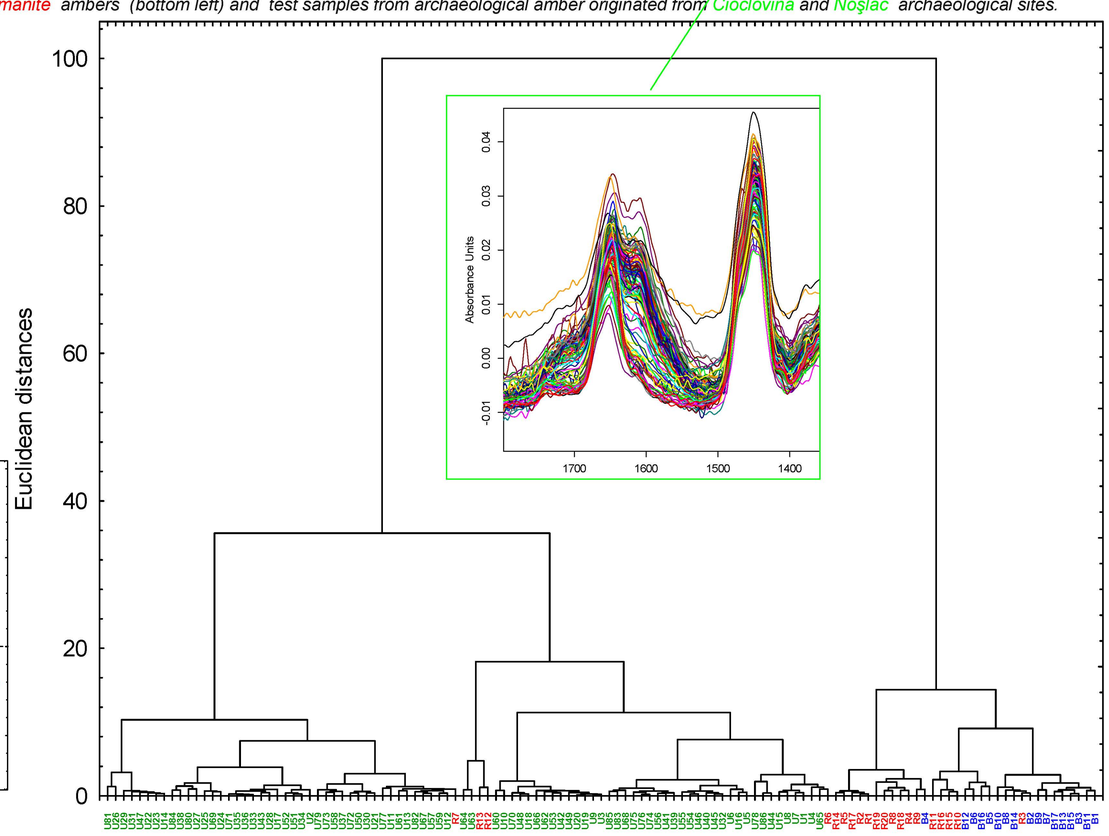


Figure 3. Multivariate Data Analysis results for 1400 - 1700 cm^{-1} FT-Raman spectral region: Principal Components Analysis (left) and Cluster Analysis (right).

RESULTS

According to the analyses performed on controlled origin Rumanite and Baltic ambers it is clear that the two fossil resins may be distinguished from each other based on their Raman spectra. In the 1622-1602 cm^{-1} domain, Rumanite presents a characteristic shoulder, while this misses in the Baltic amber spectra. Although both ambers present an intense signal around 1450 cm^{-1}, it is very clear that the signal is split only in the case of Baltic amber (Figure 2).
Multivariate Data Analysis (MDA) was used to aid the classification because it is designed to solve large-sized problems, in our case over 75 wavenumbers (1400 - 1700 cm^{-1}) designated as variables, while providing visual aid for the classification of variables and cases. The Principal Components Analysis (PCA) was carried out via the correlation matrix, while the Cluster Analysis was performed by using Ward's method in Statistica software (figure 3), with successful discrimination between Rumanite and Baltic ambers (see also table 1).

CONCLUSIONS

Preliminary results are promising and suggest that FT-Raman has good potential for discriminating between Rumanite and Baltic ambers especially when used together with Multivariate exploratory Data Analysis techniques.

REFERENCES

H.G.M. Edwards, D.W. Farwell, *Spectrochimica Acta Part A* 1996; **52**:1119
R.H. Brody, H.G.M. Edwards, A.M. Pollard, *Spectrochimica Acta Part A* 2001; **57**:1325
W. Winkler, E.C. Kirchner, A. Asenbaum, M. Musso, *J. Raman Spectrosc.* 2001; **32**: 59
J. Jehlicka, S.E. Jorge Villar, H.G.M. Edwards, *J. Raman Spectrosc.* 2004; **35**: 761
C.W. Beck, *Applied Spectroscopy Reviews* 1986; **22**: 57
I. Angelini, P. Bellintani, *Archaeometry* 2005; **47**: 441
E.D. Teodor, S.C. Litescu, A. Neacsu, G. Truica, C. Albu, *Cent. Eur. J. Chem.* 2009; **7(3)**: 560

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