The use of FTIR in the study of Romanian amber (ROMANIT)

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Introduction

In Romanian museum collections amber is present either as such (fossil resin pieces) in natural history and geological museums or processed, in jewelleries, as part of archaeological, historical and decorative art collections. Within the latter, rich collections of archaeological adornment items are preserved in the National Museum of Romanian History (MNIR), most of them recovered from funerary contexts. Identifying the origin of amber in these pieces, local versus imported (and even more, where from?), together with historical and artistic criteria, could bring important information on where, when and why a certain item was processed.
Last year, MNIR took the initiative to bring together several institutions interested in the study of Romanian amber in a project aiming to establish an analytical protocol which may distinguish the Romanian amber among the other fossil resins. The project, *"Prestige and Power. Romanian Museums' Antique Items of Trade. Non-metallic adornments, with an archaeometrical study regarding the origin of amber beads"* www.romanit.ro is financed by the Ministry of Education, Research, and Youth through t he National Centre for Projects Management (CNMP).

Romanian amber (romanit, rümanit)

The earliest mention of Romanian amber was in 1777, while the first studies on this subject, comparing Romanian with Baltic amber, date from the last decade of the 19th century [Stefanescu 1890, Istrati 1895-1898]. In the same period the German researcher Helm proposed the name „rumanite" [Stout, 2000]. The heaviest concentration of Romanian amber is in Buzau district and especially in Colti. It is supposed that river transport has redistributed the resin from this central source into other areas in Romania (Figure 1).
Amber was exploitated in Colti from 1902, while after 1937, the mines slowly cease to function and later on only the local continued to seek "the sun-stone". An "Amber Museum" was established at Colti in 1973 (Figure 2), exhibiting a wide range of fossil resins and jewelleries, in hues from opaque black to shiny yellow. The geological age of Romanian amber has been given as early as the Cretaceous and as late as Miocene but most of it, including the deposits in Colti is Oligogene [Stout 2000]. From the chemical point of view, earlier studies classify romanit as thermally altered succinite (Baltic amber) [Stout, 2000].

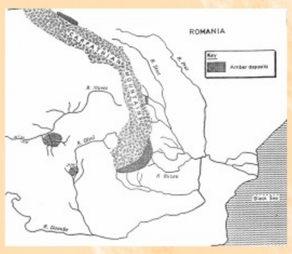


Figure 1. Amber deposits in Romania (Fraquet, 1987)

Figure 2. Amber Museum Colti, Buzau (Romania)

Analytical investigation of amber - review

Although several analytical techniques have been used in the study oh amber - Py/GC/MS [Shedrinsky 1989/90/91, Stout 2000], ^{1}H-NMR and ^{13}C-NMR [Lambert 1982/86] - infrared spectroscopy remains the most widely used and practical method for the structural characterisation and discrimination of amber types [Beck 1964/86, Thickett 1995, Angelini 2005, Guiliano 2006].
From the above mentioned studies it is clear that Baltic amber (succinite) could be identified among other fossil resins by a single carbon-oxygen deformation band near 1150 cm^{-1}, which is preceded by a broad shoulder between 1250 and 1175 cm^{-1}. This characteristic „Baltic shoulder" is perfectly horizontal in well preserved succinite but assumes an increasly negative slope in samples that have been subject to atmospheric oxidation. It is not found in any non-Baltic fossil resins, including those containing succinic acid. [Beck 1986]. It should be noted that only uncontaminated samples could be used in provenience analysis. [Thickett 1995]
Romanian amber was also characterised according to its FTIR spectra (Figure 3) while Py/GC/MS was used to identify romanit as thermally altered succinite [Stout 2000].
The present work is intended to build a methodology capable to distinguish on-site romanit among other fossil resins, based on the existing information mentioned above.

Experimental

Spectra were obtained using a Bruker Optics Tensor 27 Spectrometer, controlled by Opus 4.2. Spectra were recorded in transmission, aquired between 4000 and 400 cm^{-1} with 32 scans and a spectral resolution of 4 cm^{-1}. Samples weighting ~ 1mg were powdered, mixed with KBr and pressed in 3mm diameter pellets.
A total of 45 samples were analysed (see Table), 24 described as romanit, 18 as succinite, 2 as German amber (from Betterfeld) and 1 as Hungarian amber. Except for the latter, they were offered to us by MNIR, coordonator of ROMANIT project. All the 24 samples described as romanit origin from Buzau area, Romania while the 18 succinite samples procced from Latvia (12 samples), Poland (2 samples) and Kaliningrad (4 samples). 6 spectra from the IRUG database (5 Baltic amber and 1 described as "non-Baltic") were also included in the study.

Results and discussion

The Baltic horizontal shoulder at 1250-1175 cm^{-1} and the strong signal at 1150 cm^{-1} are very well evidenced in all the 18 spectra described as Baltic amber analysed (Figure 4), which is in very good correspondence with literature. However, from the 5 samples named "Baltic amber" on the IRUG website only one clearly presents the shoulder (IRUG NR035) while for 3 others the S/N is quite low (spectra collected in reflectance) to unambiguously see the horizontal shoulder. The IRUG NR103 described as "Baltic" do not present the Baltic shoulder (Figure 5). In 3 samples (noted with X* in the table) the slope decreases from 1250 to 1175 cm^{-1}, suggesting samples have been subject to atmospheric oxidation (see above).
From a total of 24 samples described as romanit, all but one (sample 314, Figure 7) present a strong signal at 1158 cm^{-1} while in the place corresponding to "Baltic shoulder" there is a signal with maximum at 1241 cm^{-1} (Figure 6) which very well corresponds to the spectra reported by Angelini. The Baltic shoulder is also present in Betterfeld Germany and Resolu Hungary amber. (Figure 7). IRUG NR066 spectra corresponding to "non-Baltic" amber also presents the "romanit" signal at 1158 cm^{-1} (Figure 8).
In none of the spectra corresponding to romanit samples the metilen exocyclic bands at 3076, 1644 şi 887 cm^{-1}, mentioned by Thickett as typical for amber, are present. They appear in all the other amber spectra in the table (18 Baltic ambers + 2 Betterfeld, Germany), not in IRUG NR035 (described as "Baltic") and in Resolu, Hungary (Figure 9).These bands are also absent in the archaeological ambers from northern Italy, described by Angelini.
Recent studies showed that the exocyclic bands typical for succinit decrease and finally disappear during thermal treatment [Guiliano 2006], while romanit was characterised as "thermally altered succinite" [Stout 2000]. These could well explain the absence of the above mentioned bands in romanit.

Sample	Area of origin	S/R	Baltic shoulder	3076 cm^{-1}	1644 cm^{-1}	887 cm^{-1}
105	Colti, Romania	R	--	--	--	--
109	Colti, Romania	R	--	--	--	--
129	Colti, Romania	R	--	--	--	--
140	Colti, Romania	R	--	--	--	--
146	Colti, Romania	R	--	--	--	--
153	Colti, Romania	R	--	--	--	--
169	Colti, Romania	R	--	--	--	--
179	Colti, Romania	R	--	--	--	--
182	Colti, Romania	R	--	--	--	--
185	Colti, Romania	R	--	--	--	--
277	Colti, Romania	R	--	--	--	--
282	Colti Patarlagele, Romania	R	--	--	--	--
290	Colti Patarlagele, Romania	R	--	--	--	--
292	Colti, Romania	R	--	--	--	--
305	Sibiciul de Jos, Romania	R	--	--	--	--
312	Sibiciul de Jos, Romania	R	--	--	--	--
314	Colti Patarlagele (gallery), Romania	R	X	--	--	--
317	Colti Patarlagele (gallery), Romania	R	--	--	--	--
367	Colti Patarlagele, Romania	R	--	--	--	--
368	Colti Patarlagele, Romania	R	--	--	--	--
374	Colti Patarlagele, Romania	R	--	--	--	--
377	Colti Patarlagele, Romania	R	--	--	--	--
384	Colti Patarlagele, Romania	R	--	--	--	--
388	Colti Patarlagele, Romania	R	--	--	--	--
328	Poland	S	X	X	X	X
7	Riga, Latvia	S	X	X	X	X
12	Riga, Latvia	S	X	X	X	X
17	Riga, Latvia	S	X	X	X	X
31	Riga, Latvia	S	X	X	X	X
39	Riga, Latvia	S	X	X	X	X
62	Riga, Latvia	S	X	X	X	X
64	Riga, Latvia	S	X	X	X	X
73	Riga, Latvia	S	X	X	X	X
79	Riga, Latvia	S	X	X	X	X
84	Riga, Latvia	S	X	X	X	X
297	Palanga, Lithuania	S	X	X	X	X
299	Palanga, Lithuania	S	X	X	X	X
332	Poland	S	X*	X	X	X
336	Kaliningrad (Konigsberg)	S	X*	X	X	X
338	Kaliningrad (Konigsberg)	S	X*	X	X	X
346	Kaliningrad (Konigsberg)	S	X	X	X	X
347	Kaliningrad (Konigsberg)	S	X	X	X	X
IRUG NR035	"Baltic"	S	X	--	--	--
IRUG NR103	"Baltic Sea"	S	--	X	X	X
IRUG NR212	"Baltic, succinite from Denmark"	S	X**	X	X	X
IRUG NR213	"Baltic, succinite from Denmark"	S	X**	X	X	X
IRUG NR214	"Baltic, succinite"	S	X**	X	X	X
IRUG NR066	"non Baltic"		--	X	X	X
356	Betterfeld, Germany		X	X	X	X
359	Betterfeld, Germany		X	X	X	X
	Resolu, Hungary		X	--	--	--

Table 1. Samples description and results (notes: S=succinite R=romanit; X=present; -- = absent; X = Baltic shoulder present with decreasing slope from 1250 to 1175 cm^{-1} ; ** Baltic shoulder not well evidenced, S/N low, spectra collected in reflectance)*

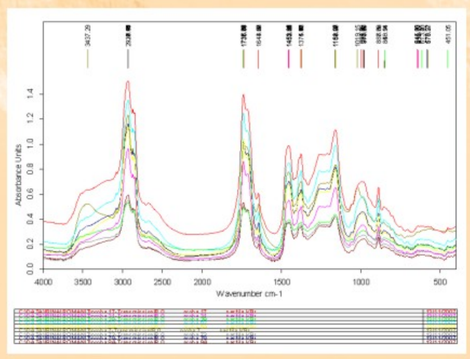


Figure 4. FTIR spectra for samples described as succinite (Baltic amber)

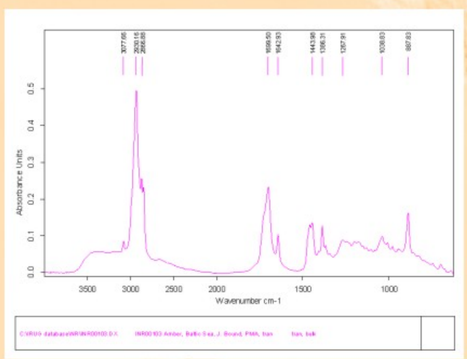


Figure 5. IRUG NR103 described as "Baltic" not presenting the Baltic shoulder

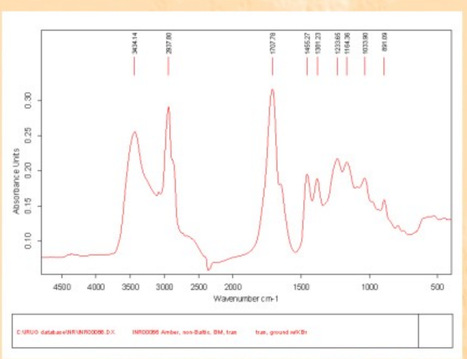


Figure 8. IRUG NR066 described as "non-Baltic" presenting the "romanit" signal at 1158 cm^{-1}

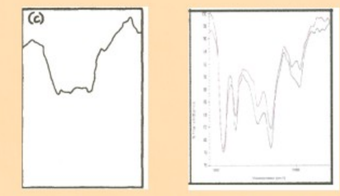
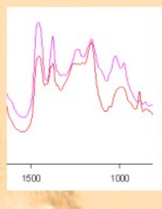


Figure 3. Spectra of romanit. Detail on the area between 1600 - 1000 cm^{-1} typical to distinguish romanit among other fossil resins. (Beck, 1986 - left; Angelini, 2005 - right)



Spectra of romanit (violet) and succinit (red). Detail on the area between 1600 - 1000 cm^{-1}

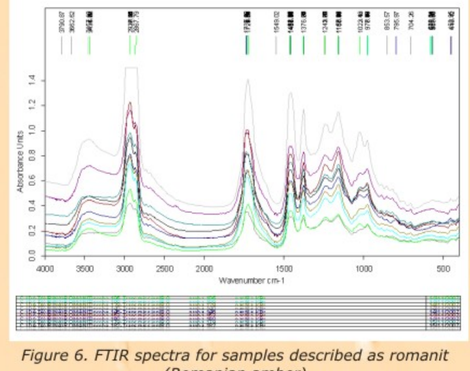


Figure 6. FTIR spectra for samples described as romanit (Romanian amber)

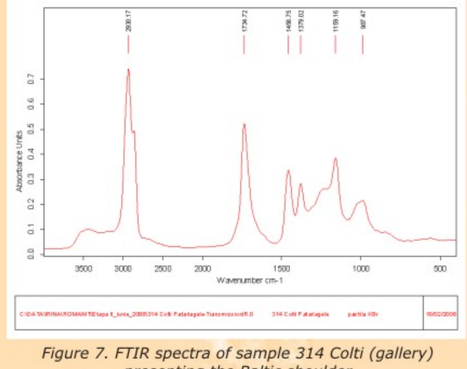


Figure 7. FTIR spectra of sample 314 Colti (gallery) presenting the Baltic shoulder

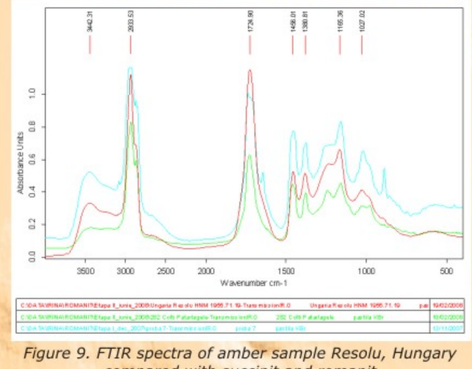


Figure 9. FTIR spectra of amber sample Resolu, Hungary compared with succinit and romanit

Conclusion

The present analysis, interpreted according to the results published by other researchers, showed that Romanian amber could be well characterised by the FTIR spectra, as it presents a typical strong signal at 1158 cm^{-1}, which is not present in other fossil resins. The exocyclic bands at 3076, 1644, 887 cm^{-1} typical for succinit are not present in romanit FTIR spectra.

References

Angelini, I., Bellintani P., Archaeological ambers from Northern Italy: an FTIR-DRIFT study of provenance by comparison with the geological amber database, *Archaeometry* 47, 2005, 441-454.
Beck C. W., Spectroscopic Investigations of Amber, *Applied Spectroscopy Reviews*, 22:1, 57-110
Fraquet H., Amber. Buterworths, London
Guiliano M. et all., Applications of diamond crystal ATR FTIR spectroscopy to the characterization of ambers, *Spectrochimica Acta A Mol. Biomol. Spectrosc.,* 2006, article in press
Istrati C., Rumanitul sau succinul din Romania, *Bul. Soc. Sci.* Bucuresti 4, 1895, 59-77, La Roumanite ou le Succin de Roumanie *Ana. Acad. Rom.* 16, 55-77
Neacsu A., 2007, ROMANIT internal report
Stout, E.C., Beck C. W., Anderson K. B.: Identification of Rumanite (Romanian Amber) as thermally altered succinite, *Phys. Chem. Minerals*, 27, 2000, 665-678.
Thickett D. & al The Conservation of Amber, *Studies in Conservation* 40, 1995, 217-226

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