The Chemical Identification of Resinated Wine and a Mixed Fermented Beverage in Bronze-Age Pottery Vessels of Greece

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Archaeological Chemistry – or what can be more romantically termed Molecular Archaeology – holds out the promise of opening up whole new vistas on the ancient world. Unlike textual, pictorial or ethnoarchaeological inferences, the power of Molecular Archaeology lies in its providing direct, contemporaneous, non-tendentious evidence of ancient activities. In the last several decades, highly sensitive instruments have become routinely available to detect milligram, even microgram, quantities of ancient organic materials (see Biers and McGovern 1990; McGovern 1995 and 2003). Ancient earthenware pottery, made from aluminosilicate clays, were porous enough to absorb the ancient organics, especially in the liquid state, and hold them relatively intact for millennia. Much has been written about pottery typology, dating and cultural interpretation, but until the advent of the new Molecular Archaeological tools, it was virtually impossible to determine what a vessel actually contained. Once having established that, it becomes possible to reconstruct ancient cuisines, social and religious practices, economic activities, and much more in a convincing fashion.

The prospects are not equally good for all organic compounds, since some easily degrade and others may have been washed out from the pottery in an acid bath. Contamination from plastic containers (see C. Beck, *et al.*, p. 14; Martlew p. 236) or well-intentioned conservation efforts may also conspire to conceal the original organics. Nevertheless, the prospects are now very good for tracking down the natural source – whether plant or animal – for the ancient organic compounds that are identified. Royal Purple dye (6,6'-dibromoindigotin) is one example of an extremely stable compound, due to its resonance structure, that can survive intact for millennia and is highly specific for a family of marine mollusks (McGovern and Michel 1990).

I. Background to the Investigation and Experimental Methods

The analyses reported on in this paper provide the detailed evidence for the conclusions presented in the catalogue (Tzedakis and Martlew 1999) for the exhibition, "Minoans and Mycenaeans Flavours of Their Time." The Molecular Archaeology Laboratory of the Museum Applied Science Center for Archaeology (MASCA) at the University of Pennsylvania Museum generally employs three complementary chemical techniques to detect organic compounds present in ancient fermented beverages (see McGovern 1997, 1998 and 2000a; McGovern and Michel 1993 and 1995; Michel, *et al.* 1992; and McGovern, *et al.* 1996, 1997 and 1999). By 2004, our capabilities had expanded to include liquid and gas chromatography-mass spectrometry (LC-MS and GC-MS) on a routine basis (e.g., McGovern, *et al.* 2004).

1. Diffuse-Reflectance Infrared Fourier-Transform Spectrometry (DRIFTS)

DRIFTS has been the "work horse" of the MASCA Molecular Archaeology program. This method takes advantage of the nature of chemical bonds to stretch and bend when they absorb infrared (IR) light. Each chemical compound absorbs infrared light at specific frequencies which can be precisely measured and shown on a spectrum. The technique is extremely versatile and precise, requiring as little as a milligram of material. At the time of the analyses, our laboratory used a Nicolet 5 DXB FT-IR spectrometer, with OMNIC 3.0 software and search capabilities. Spectra were deresolved at 8 cm^{-1} wavenumber, a frequency unit used by spectroscopists, for library storage, searches, and printing.

The sample, which was obtained by extracting the ancient pottery sherd twice with a boiling organic solvent (typically, methanol and/or chloroform) for 20 min each and evaporating to dryness, is ground up together with the transparent solid, potassium bromide. The sample is then subjected to multiple passes of IR light that are rapidly reflected off the sample and recombined with the reference beam by a moving mirror, to yield an "interferogram." After Fourier-transform processing, the "interferogram" provides a very precise absorption spectrum for the ancient sample, with minimal background noise.

Any Molecular Archaeological project involves building up a large database of modern reference materials and standards, to be compared with the ancient "unknown" sample. Even ancient samples, which can be unequivocally identified as being pure, may serve as reference standards. Other databases from other laboratories provide spectra for additional compounds, including common foods, drugs, and other materials that were also consumed or used in antiquity, and the combined databases are searched to find the best "match" for the "unknown." Depending on how closely the absorption peaks coincide with one another and how similar in shape and multiplicity they are, the "unknown" sample can be variously identified: whether a single compound, a mixture of compounds, or being dominated by specific chemical groups that might belong to any number of compounds. Because the whole sample is analyzed simultaneously, the absorption peaks of individual compounds often overlap, sometimes frustrating accurate identifications. For example, various tree resins, tartaric acid, and beeswax have carbonyl absorptions in the vicinity of 1740 and 1720/1710 cm^{-1}. However, the natural products and compounds can be partly distinguished by examining their spectra for greater complexity in the carbonyl region above 1740 cm^{-1} (most indicative of a tree resin) or in the carbonyl region below 1720/1710 cm^{-1} (most indicative of beeswax). Other inferences can be arrived at by comparing individual sample spectra with the frequency assignments and their most probable interpretation in Tables 1 and 2.

2. High-Performance Liquid Chromatography (HPLC)

For unambiguous identifications, the compounds in a mixed material are most efficiently separated by a technique called chromatography. HPLC, in principal, is very simple: the "unknown" ancient sample is dissolved in a suitable organic solvent, which is then passed through a column that is lined with a material that preferentially absorbs the compounds of interest. Depending on how strong the affinity is between the compound, moving solvent, and stationary substrate, the compound will take more or less time to pass through column. The goal is to separate the "unknown" into its component constituents, which can then be identified by another analytical technique (whether ultraviolet (UV)-visible spectrometry, mass spectrometry, nuclear magnetic resonance, etc.).

MASCA's Molecular Archaeology Laboratory uses a Hewlett-Packard 1090 Liquid Chromatograph with an A06.01 ChemStation. Microgram amounts are analyzed. HPLC uses stainless steel separation columns of various lengths that have uniform and extremely fine particles (3–10 μ), with a very large surface area, fused to their interiors. Under high pressures (typically, our instrument is run at 80 atmospheres or about 1200 $lbs/inch^2$), very small samples (usually 10 or 20 μl) can be efficiently separated. The goal, which is not always that easy and sometimes as much art as science, is to select the right conditions to separate fully all the components of an unknown archaeological sample.

As the various components come off the separation column, they are fed into a UV-visible spectrophotometer diode array, ideally yielding characteristic absorptions of chromophores by the compounds of interest. In the UV part of the electromagnetic spectrum, valence electrons and double bonds are particularly susceptible to excitation. As the number of double bonds increase, the absorption shifts more and more to the visible range, as best illustrated by dye molecules (for example, indigotin and alizarin). The UV-visible absorption spectrum is generally not as informative as IR analysis or mass spectrometry, but, combined with a good separation of compounds, it can provide excellent evidence for, or corroboration of, specific compounds.

Our typical HPLC experimental set-up, which was used for the Greek Bronze Age pottery, was to run a methanol extract of the sample through a silicic acid column (Supelco Supercosil LC-Si). This column has relatively polar silica particles with adsorbed water. We use a column that is 25 cm. in length and 4.6 mm. in diameter. The sample is dissolved in methanol, which also serves as the mobile phase, and moves through the column at 2 ml/min. This is a fairly rapid flow rate, and the whole sample comes off the column in less than 3 min. We are particularly interested in polar compounds, and methanol extraction and the polar column enable us to isolate and test for those compounds. Liquid chromatography is rapidly becoming the main tool of biochemical research generally, even more so than gas chromatography, because many more compounds can be dissolved in a solvent than can be volatilized.

The MASCA laboratory has built up an HPLC database of several hundred relevant archaeological samples and modern reference compounds. The ChemStation software searches the database for the best matches for a UV spectrum at a specific retention time, which is typically monitored at 210 nm.

Table 1 Chemical data for resinated wine samples

				Feigl Spot Test		Infrared Spectrometry			High-Performance Liquid Chromatography		
Site	Sample # (EUM-)	Period (Date)	Type	Tartrate	Oxalate	Frequency (cm^{-1})	Assignment	Compound/ Natural Product	Retention Time (min)	Best Matches	Compound/ Natural Product
Myrtos	**95**	Early Minoan IIB (ca. 2200 B.C.)	Pithos	+	-	3440	OH stretch	Acid or water of hydration	1.54	Chania EUM-47	resinated wine
						2920	Long chain CH_2 stretch	Resin		Mycenae EUM-195	resinated wine
						2850	Long chain CH_2 stretch	Resin		Hajji Firuz Tepe	resinated wine
						1750 sh	Carbonyl stretch	Resin			
						1730	Carbonyl stretch	Tartaric acid/Resin			
						1710	Carbonyl stretch	Tartaric acid/Resin			
						1685 sh	Carbonyl stretch	Resin			
						1635	Carbonyl stretch	Tartrate			
						1585	Carbonyl stretch	Tartrate			
						1550	Carbonyl stretch	Tartaric acid/Resin			
						1525					
						1465	OH bend	Resin			
						1445	OH bend	Tartaric acid			
						1405					
						1380	CO_2^- sym stretch	Resin/Tartrate			
						1350					
						1250 broad	CO stretch	Tartaric acid/Resin			
						735	Long chain CH_2 bend	Beeswax			
Myrtos	**97**	Early Minoan IIB (ca. 2200 B.C.)	Pithos	Borderline	not run	3410	OH stretch	Acid or water of hydration	1.58	Myrtos EUM-98	see below
						3235	OH stretch	Acid or water of hydration		Uluburun 144	terebinth tree resin
						2960	Long chain CH_2 stretch	Resin			
						2920	Long chain CH_2 stretch	Resin			
						2855	Long chain CH_2 stretch	Resin			
						2195	Carbonyl stretch	Atmospheric CO_2			
						1745 sh	Carbonyl stretch	Resin			
						1635	Carbonyl stretch	Tartrate			
						1585	Carbonyl stretch	Tartrate			
						1540 sh	Carbonyl stretch				
						1460	OH bend	Resin			
						1365	CO_2^- sym stretch	Tartrate			
						1325					
Myrtos	**98**	Early Minoan IIB (ca. 2200 B.C.)	Pithos	+	not run	3411	OH stretch	Acid or water of hydration	1.58	Myrtos EUM-97	see below
						3410	OH stretch	Acid or water of hydration		Uluburun 144	terebinth tree resin
						2920	Long chain CH_2 stretch	Resin			
						2850	Long chain CH_2 stretch	Resin			
						1730 sh	Carbonyl stretch	Tartaric acid			
						1705	Carbonyl stretch	Tartaric acid			
						1635	Carbonyl stretch	Tartrate			
						1545	Carbonyl stretch	Tartrate			
						1460	OH bend	Resin			
						1435	OH bend	Tartaric acid			
						1420		Tartrate			
						1250 broad	CO stretch	Tartaric acid/Resin			
Myrtos	**99**	Early Minoan IIB (ca. 2200 B.C.)	Pithos	+	not run	3355	OH stretch	Acid or water of hydration	1.54	Myrtos EUM-104	see below
						2960	Long chain CH_2 stretch	Resin		Chania-Kastelli EUM-67	see Table 2
						2920	Long chain CH_2 stretch	Resin		modern pine resin	pine resin
						2855	Long chain CH_2 stretch	Resin			
						2356	Carbonyl stretch	Atmospheric CO_2			
						2325	Carbonyl stretch	Atmospheric CO_2			
						1735	Carbonyl stretch	Tartaric acid or resin			
Myrtos	**99 cont.**					1695	Carbonyl stretch	Resin			
						1635	Carbonyl stretch	Tartrate			
						1610	Carbonyl stretch	Resin/Tartrate			
						1580	Carbonyl stretch	Resin/Tartrate			
						1540	Carbonyl stretch				
						1465	OH bend	Resin			
						1435	OH bend	Tartaric acid			
						1385 broad	CO_2^- sym stretch	Tartrate/Resin			
						1280	CO stretch	Resin			
						1250	CO stretch	Tartaric acid			
						1180					
						725	Long chain CH_2 bend	Beeswax			

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				Feigl Spot Test		Infrared Spectrometry			High-Performance Liquid Chromatography		
Site	Sample # (EUM-)	Period (Date)	Type	Tartrate	Oxalate	Frequency (cm^{-1})	Assignment	Compound/ Natural Product	Retention Time (min)	Best Matches	Compound/ Natural Product
Myrtos	**100**	Early Minoan IIB (ca. 2200 B.C.)	Pithos	+	Borderline	3435	OH stretch	Acid or water of hydration	1.55	calcium oxalate	possibly barley beer
						3240	OH stretch	Acid or water of hydration		Malkata organic sample #10	probably barley beer
						2960	Long chain CH_2 stretch	Resin			
						2920	Long chain CH_2 stretch	Resin			
						2855	Long chain CH_2 stretch	Resin			
						2150	Carbonyl stretch	Atmospheric CO_2			
						1635	Carbonyl stretch	Tartrate			
						1545	Carbonyl stretch	Tartrate			
						1465	OH bend	Resin			
Myrtos	**104**	Early Minoan IIB (ca. 2200 B.C.)	Pithos	+	+	too small for IR			1.63	modern pine resin	pine resin
										Uluburun 102	terebinth tree resin
Monastiraki	**30**	Middle Minoan IIB (ca. 1700 B.C.)	Cooking Pot	Borderline	not run	3425	OH stretch	Acid or water of hydration	1.56	Mycenae EUM-195	see below
						3240	OH stretch	Acid or water of hydration		Tell el-Dab`a JH082	resinated wine
						2960	Long chain CH_2 stretch	Resin		Tell el-Dab`a no. 7648M	resinated wine
						2925	Long chain CH_2 stretch	Resin		Susa (Louvre Sb18869)	resinated wine
						2355	Carbonyl stretch	Atmospheric CO_2			
						2165	Carbonyl stretch	Atmospheric CO_2			
						1715 sh	Carbonyl stretch	Resin			
						1635	Carbonyl stretch	Tartrate			
						1460	OH bend	Resin			
						1420		Tartrate			
						1380	CO_2^- sym stretch	Tartrate/Resin			
						1280	CO stretch	Tartrate			
Monastiraki	**136**	Middle Minoan IIB (ca. 1700 B.C.)	Pithos	Borderline	not run	3425	OH stretch	Acid or water of hydration	1.59	Tell el-Dab`a grape-treading installation	grape
						3230	OH stretch	Acid or water of hydration			
						2960	Long chain CH_2 stretch	Resin			
						2915	Long chain CH_2 stretch	Resin			
						2855	Long chain CH_2 stretch	Resin			
						2360	Carbonyl stretch	Atmospheric CO_2			
						2335	Carbonyl stretch	Atmospheric CO_2			
						1735	Carbonyl stretch	Tartaric acid/Resin			
						1705 sh	Carbonyl stretch	Tartaric acid/Resin			
						1635	Carbonyl stretch	Tartrate			
						1590 sh	Carbonyl stretch	Tartrate			
						1555	Carbonyl stretch	Tartrate			
						1540	Carbonyl stretch				
						1470	OH bend	Resin			
						1455	OH bend	Tartaric acid			
						1420		Tartrate			
						1365	CO_2^- sym stretch	Tartrate/Resin			
						1260 broad	CO stretch	Tartrate/Resin			
Apodoulou	**148**	Middle Minoan IIB (ca. 1900-1700 B.C.)	Conical Cup	+	not run	too small for IR			1.56	Tell el-Dab`a no. 7648M	resinated wine
										Tell el-Dab`a grape-treading installation	grape
Mycenae	**67**	Mycenaean IIIB1 (ca. 1340-1250 B.C.)	Amphora	+	not run	3435	OH stretch	Acid or water of hydration	1.55	Susa (Louvre Sb18869)	resinated wine
						2965	Long chain CH_2 stretch	Resin		Chamalevri EUM-180	see Table 2
						2925	Long chain CH_2 stretch	Resin		many Near Eastern resinated wine samples	
						2850	Long chain CH_2 stretch	Resin			
						2710					
						2365	Carbonyl stretch	Atmospheric CO_2			
						2330	Carbonyl stretch	Atmospheric CO_2			
						1740	Carbonyl stretch	Tartaric acid/Resin			
						1710 sh	Carbonyl stretch	Tartaric acid/Resin			
						1605	Carbonyl stretch	Tartrate			
						1560	Carbonyl stretch	Tartrate			
						1465	OH bend	Resin			
						1445	OH bend	Tartaric acid			
						1420		Tartrate			
						1385	CO_2^- sym stretch	Tartrate/Resin			
						1260 broad	CO stretch	Tartrate/Resin			
						725	Long chain CH_2 bend	Beeswax			

Table 2 Chemical data for mixed fermented beverages

				Feigl Spot Test		Infrared Spectrometry			High-Performance Liquid Chromatography		
Site	Sample # (EUM-)	Period (Date)	Type	Tartrate	Oxalate	Frequency (cm^{-1})	Assignment	Compound/ Natural Product	Retention Time (min)	Best Matches	Compound/ Natural Product
Chania-Splanzia	**36**	Late Minoan IA (ca. 1600-1480 B.C.)	Conical Cup	+	+	too small for IR			1.55 and 1.62	many Near Eastern resinated wine samples	mixed fermented beverage
										Midas Tumulus MM45	mixed fermented beverage
										Midas Tumulus MM104	mixed fermented beverage
Chania-Splanzia	**47**	Late Minoan IA (ca. 1600-1480 B.C.)	Conical Cup	+	not run	3355	OH stretch	Acid or water of hydration	1.52 and 1.61	Midas Tumulus MM128	see below
						2965	Long chain CH_2 stretch	Resin		Armenoi EUM-111	
						2920	Long chain CH_2 stretch	Resin		many Greek, Near Eastern & Egyptian wine samples	
						2855	Long chain CH_2 stretch	Resin			
						2360	Carbonyl stretch	Atmospheric CO_2		Midas Tumulus MM45	mixed fermented beverage
						2330	Carbonyl stretch	Atmospheric CO_2		Uluburun 102	terebinth tree resin
						1770 sh	Carbonyl stretch	Resin		Uluburun 215	terebinth tree resin
						1735	Carbonyl stretch	Tartaric acid/Resin/Beeswax			
						1720	Carbonyl stretch	Tartaric acid/Resin/Beeswax			
						1700	Carbonyl stretch	Possibly resin			
						1680	Carbonyl stretch	Possibly resin			
						1650	Carbonyl stretch	Possibly tartrate			
						1620	Carbonyl stretch	Resin			
						1540	Carbonyl stretch				
						1455	OH bend	Tartaric acid/Resin			
						1420		Tartrate			
						1390	CO_2^- sym stretch	Resin/Tartrate			
						1370	CO_2^- sym stretch	Resin/Tartrate			
						1165		Beeswax			
Chania-Splanzia	**58**	Late Minoan IA (ca. 1600-1480 B.C.)	Conical Cup	+	Borderline	3370	OH stretch	Acid or water of hydration	1.52 and 1.62	Chania EUM-36	see above
						2960	Long chain CH_2 stretch	Resin/Beeswax		Chania EUM-47	see above
						2910	Long chain CH_2 stretch	Resin/Beeswax		Chania EUM-61	see below
						2850	Long chain CH_2 stretch	Resin/Beeswax		Armenoi EUM-111	see below
						1730	Carbonyl stretch	Tartaric acid/Beeswax/Resin		many Greek & Near Eastern resinated wine samples	
						1705	Carbonyl stretch	Tartaric acid/Beeswax/Resin			
						1660	Carbonyl stretch	Resin		Uluburun 215	terebinth tree resin
						1620	Carbonyl stretch	Resin		modern mead sample no. 5	mead
						1470	OH bend	Tartaric acid/Resin		potassium gluconate	honey
						1420		Tartrate		modern orange blossom honey	honey
						1385	CO_2^- sym stretch	Resin			
						1360					
						1250 broad	CO stretch	Tartaric acid/Resin			
						1175		Beeswax			
						720	Long chain CH_2 bend	Beeswax			
Chania-Splanzia	**61**	Late Minoan IA (ca. 1600-1480 B.C.)	Conical Cup	+	not run	3355	OH stretch	Acid or water of hydration	1.53 and 1.61	Chania EUM-36	see above
						2960	Long chain CH_2 stretch	Resin/Beeswax		Armenoi EUM-111	see below
						2920	Long chain CH_2 stretch	Resin/Beeswax		many Near Eastern resinated wine samples	
						2850	Long chain CH_2 stretch	Resin/Beeswax			
						2365	Carbonyl stretch	Atmospheric CO_2		Uluburun 102	terebinth tree resin
						2330	Carbonyl stretch	Atmospheric CO_2		Midas Tumulus MM45	mixed fermented beverage
						1735	Carbonyl stretch	Tartaric acid/Beeswax/Resin		modern mead sample no. 5	mead

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				Feigl Spot Test		Infrared Spectrometry			High-Performance Liquid Chromatography		
Site	Sample # (EUM-)	Period (Date)	Type	Tartrate	Oxalate	Frequency (cm^{-1})	Assignment	Compound/ Natural Product	Retention Time (min)	Best Matches	Compound/ Natural Product
Chania-Splanzia	61 cont.					1715 sh	Carbonyl stretch	Tartaric acid/Beeswax/Resin			
						1675	Carbonyl stretch	Resin/Oxalate			
						1605	Carbonyl stretch	Tartrate/Oxalate			
						1570	Carbonyl stretch	Tartrate			
						1545	Carbonyl stretch				
						1470	OH bend	Tartaric acid/Resin			
						1425		Tartrate			
						1380	CO_2^- sym stretch	Tartaric acid/Resin/Oxalate			
						1360					
						1250	CO stretch	Tartaric acid/Resin			
						725	Long chain CH_2 bend	Beeswax			
Chania-Kastelli	252	Late Minoan IA (ca. 1600-1480 B.C.)	Stirrup Jar	-	+	too small for IR			1.63	Tell Deir `Alla no. 3203	resinated wine
										Uluburun 215	terebinth tree resin
										modern pine resin	pine resin
										modern orange blossom honey	honey
										Midas tumulus food samples	honey, grape/wine & barley
Chania-Kastelli	267	Late Minoan IA (ca. 1600-1480 B.C.)	Stirrup Jar	-	not run	too small for IR			1.57	Chania-Kastelli EUM-252	see above
										Myrtos EUM-104	resinated wine
										modern pine resin	pine resin
										Midas tumulus food samples	honey, grape/wine & barley
Chania-Kastelli	269	Late Minoan IA (ca. 1600-1480 B.C.)	Stirrup Jar	+	+	3425	OH stretch	Acid or water of hydration	1.57	Chania-Splanzia EUM-47	see above
						2960	Long chain CH_2 stretch	Resin/Beeswax		Chania-Splanzia EUM-61	see above
						2915	Long chain CH_2 stretch	Resin/Beeswax		Midas tumulus MM51	mixed fermented beverage
						2855	Long chain CH_2 stretch	Resin/Beeswax		Malkata organic sample #8	resinated wine
						2360	Carbonyl stretch	Atmospheric CO_2			
						2330	Carbonyl stretch	Atmospheric CO_2			
						1735	Carbonyl stretch	Tartaric acid/Beeswax/Resin			
						1695	Carbonyl stretch	Resin			
						1635	Carbonyl stretch	Tartrate			
						1580	Carbonyl stretch	Tartrate			
						1545	Carbonyl stretch				
						1470	OH bend	Resin			
						1455	OH bend	Tartaric acid			
						1425		Tartrate			
						1380	CO_2^- sym stretch	Tartaric acid/Resin/Oxalate			
						1335	CO stretch	Oxalate			
						1265 broad	CO stretch	Tartaric acid/Resin			
						1175		Beeswax			
						725	Long chain CH_2 bend	Beeswax			
Armenoi	111	Late Minoan IIIA/B (ca. 1400-1200 B.C.)	Kylix	+	not run	3435	OH stretch	Acid or water of hydration	1.57 and 1.64	Midas Tumulus MM45	mixed fermented beverage
						2960	Long chain CH_2 stretch	Resin/Beeswax		Midas Tumulus MM51	mixed fermented beverage
						2915	Long chain CH_2 stretch	Resin/Beeswax		Midas Tumulus MM104	mixed fermented beverage
						2850	Long chain CH_2 stretch	Resin/Beeswax		Midas Tumulus MM128	mixed fermented beverage
						1735	Carbonyl stretch	Tartaric acid/Beeswax/Resin		many Near Eastern & Egyptian	
						1710	Carbonyl stretch	Tartaric acid/Beeswax/Resin		resinated wine samples	
						1635	Carbonyl stretch	Tartrate		potassium gluconate	honey
						1555 sh	Carbonyl stretch	Tartrate			
						1530					
						1460	OH bend	Resin			
						1440 sh	OH bend	Tartaric acid			

				Feigl Spot Test		Infrared Spectrometry			High-Performance Liquid Chromatography		
Site	Sample # (EUM-)	Period (Date)	Type	Tartrate	Oxalate	Frequency (cm^{-1})	Assignment	Compound/ Natural Product	Retention Time (min)	Best Matches	Compound/ Natural Product
Armenoi	111 cont.					1375	CO_2^- sym stretch	Tartrate/Resin			
						1175		Beeswax			
						725	Long chain CH_2 bend	Beeswax			
Armenoi	116	Late Minoan IIIA (ca. 1400-1200 B.C.)	Kylix	-	-	too small for IR			1.56 and 1.61	Chania EUM-36	see above
										many Near Eastern & Egyptian resinated wine samples	
Armenoi	121	Late Minoan IIIA (ca. 1400-1200 B.C.)	Cup	+	not run	too small for IR			1.56	Chamalevri EUM-188	see below
										many Near Eastern & Egyptian resinated wine samples	
Armenoi	122	Late Minoan IIIA (ca. 1400-1200 B.C.)	Cup	+	+	3425	OH stretch	Acid or water of hydration	1.56	Midas Tumulus MM104	mixed fermented beverage
						2960	Long chain CH_2 stretch	Resin/Beeswax		many Near Eastern & Egyptian	
						2915	Long chain CH_2 stretch	Resin/Beeswax		resinated wine samples	
						2855	Long chain CH_2 stretch	Resin/Beeswax			
						1745	Carbonyl stretch	Tartaric acid/Beeswax/Resin			
						1725	Carbonyl stretch	Tartaric acid/Beeswax/Resin			
						1705	Carbonyl stretch	Resin			
						1685	Carbonyl stretch	Resin			
						1665	Carbonyl stretch	Oxalate			
						1640	Carbonyl stretch	Tartrate			
						1625	Carbonyl stretch	Possibly resin			
						1610	Carbonyl stretch	Oxalate			
						1575	Carbonyl stretch	Tartrate			
						1545	Carbonyl stretch				
						1530					
						1505	Carbonyl stretch	Oxalate			
						1485					
						1460	OH bend	Resin			
						1445	OH bend	Tartaric acid			
						1410					
						1385	CO_2^- sym stretch	Tartrate/Resin/Oxalate			
						1360					
						1330	CO stretch	Oxalate			
						1295					
						1245	CO stretch	Tartaric acid/Resin			
						725	Long chain CH_2 bend	Beeswax			
Mycenae	195	LH IIIA2 (ca. 1370-1340 B.C.)	"Beer Mug"	Borderline	Borderline	too small for IR			1.58	many Near Eastern resinated wine samples	
										Midas Tumulus MM104	mixed fermented beverage

Site	Sample # (EUM-)	Period (Date)	Type	Feigl Spot Test: Tartrate	Feigl Spot Test: Oxalate	Infrared Spectrometry: Frequency (cm^{-1})	Infrared Spectrometry: Assignment	Infrared Spectrometry: Compound/ Natural Product	High-Performance Liquid Chromatography: Retention Time (min)	High-Performance Liquid Chromatography: Best Matches	High-Performance Liquid Chromatography: Compound/ Natural Product
Mixed Beverage or Possibly Food Samples											
Chamalevri	180	Late Minoan IIIC1	Baking Plate	+	not run	too small for IR			1.55	Mycenae EUM-180 installation	honey, grape/wine & barley
										many Near Eastern resinated wine samples	
Chamalevri	188	Late Minoan IIIC1 (ca. 1190-1130 B.C.)	Tripod Cup	+	-	3410	OH stretch	Acid or water of hydration	1.57 and 1.62	Chamalevri 180	see above
						2960	Long chain CH_2 stretch	Resin/Beeswax		Chania-Splanzia EUM-61	see above
						22915	Long chain CH_2 stretch	Resin/Beeswax		Chania-Kastelli EUM-269	see above
						2855	Long chain CH_2 stretch	Resin/Beeswax		Midas Tumulus MM51	mixed fermented beverage
						2640				Midas Tumulus MM128	mixed fermented beverage
						2360	Carbonyl stretch	Atmospheric CO_2		Midas Tumulus MM1b food samples	honey, grape/wine & barley
						2330	Carbonyl stretch	Atmospheric CO_2			
						1735	Carbonyl stretch	Tartaric acid/Beeswax/Resin			
						1715 sh	Carbonyl stretch	Tartaric acid/Beeswax/Resin			
						1700	Carbonyl stretch	Resin			
						1670	Carbonyl stretch	Resin/Oxalate			
						1630	Carbonyl stretch	Tartrate			
						1580	Carbonyl stretch	Tartrate			
						1540	Carbonyl stretch				
						1465	OH bend	Resin			
						1435	OH bend	Tartaric acid			
						1420		Tartrate			
						1375	CO_2^- sym stretch	Tartrate/Resin/Oxalate			
						1255 broad	CO stretch	Tartaric acid/Resin			
						1175		Beeswax			
						730	Long chain CH_2 bend	Beeswax			

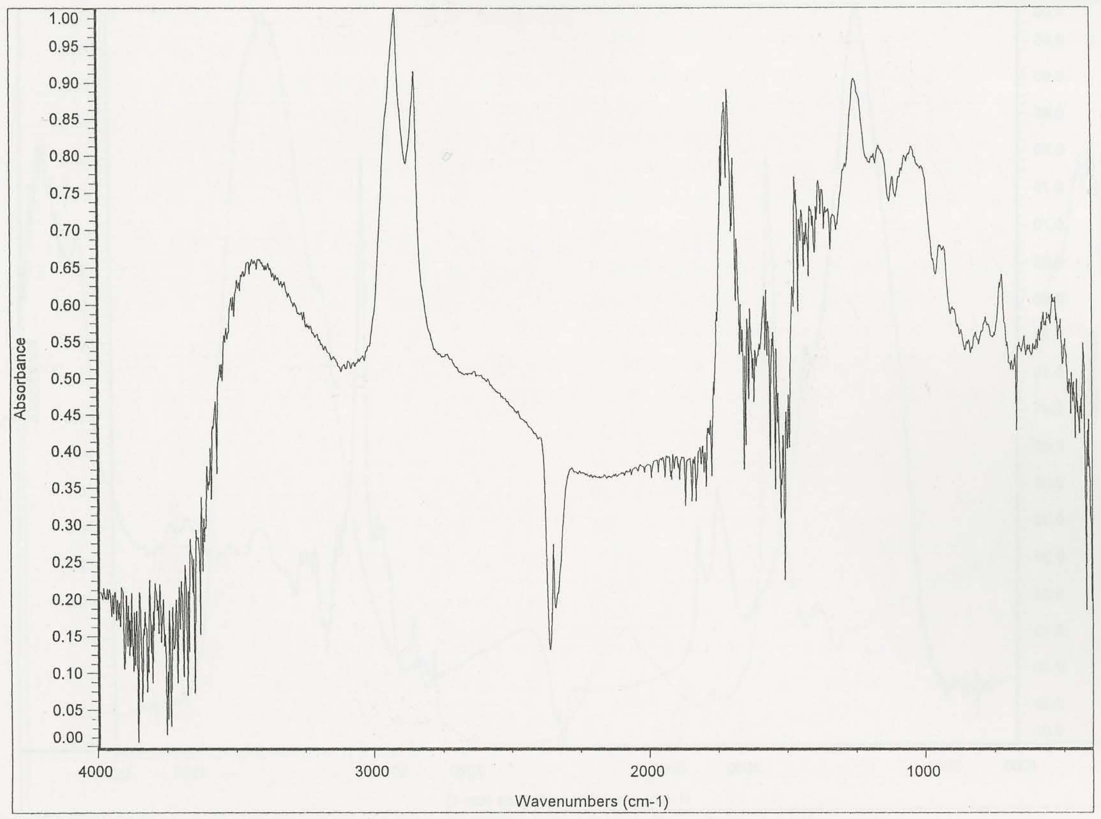

Figure 1 *Myrtos Phournou Koryphe (EUM 95): infrared spectrum*

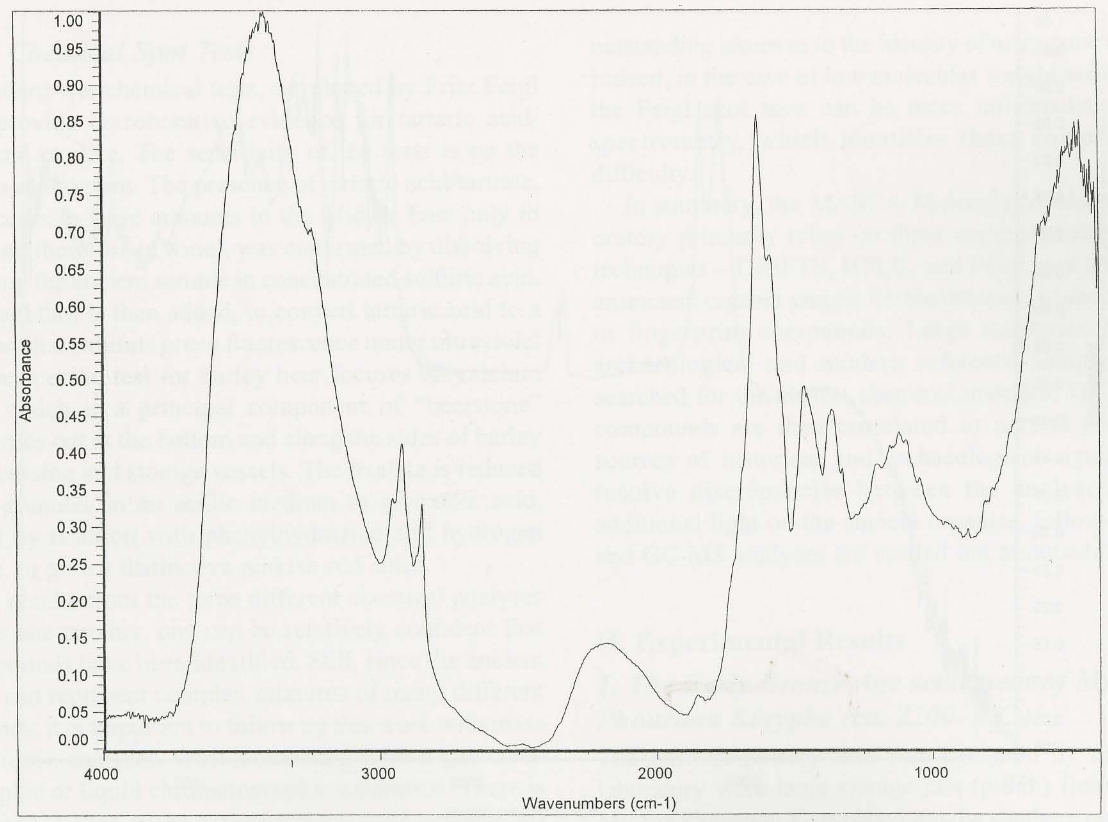

Figure 2 *Myrtos Phournou Koryphe (EUM 97): infrared spectrum*

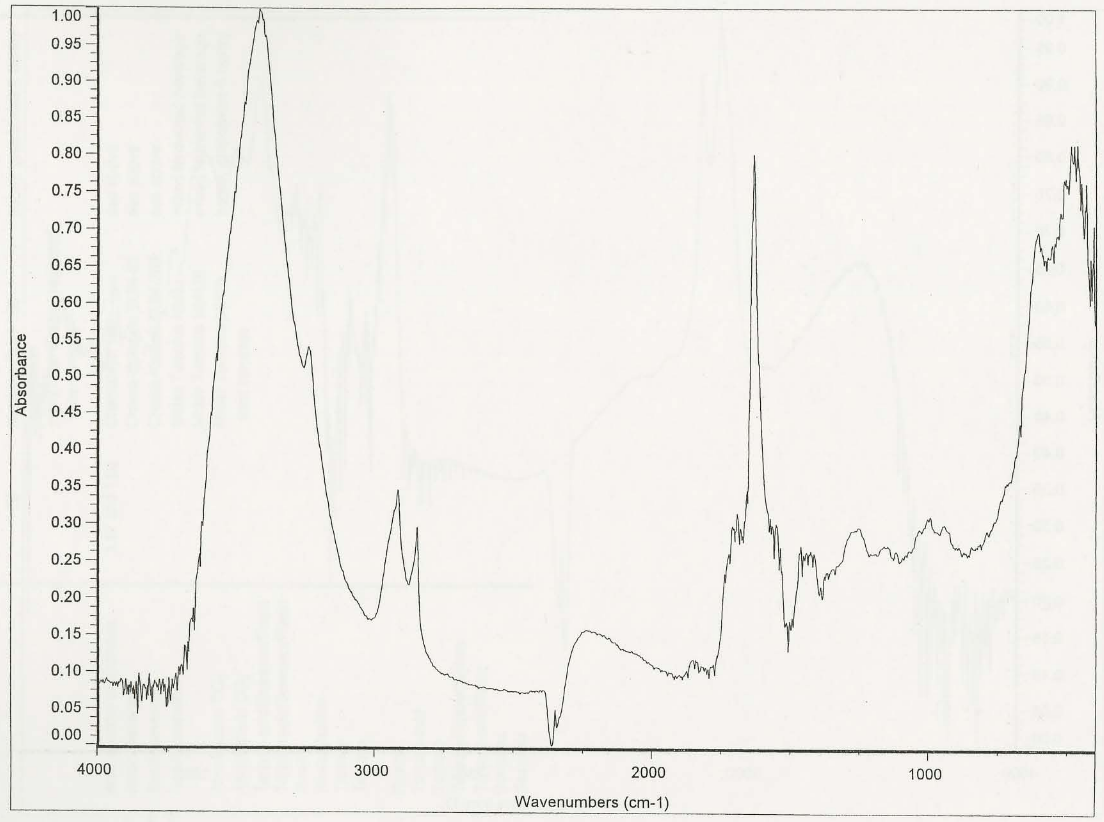

Figure 3 *Myrtos Phournou Koryphe (EUM 98): infrared spectrum*

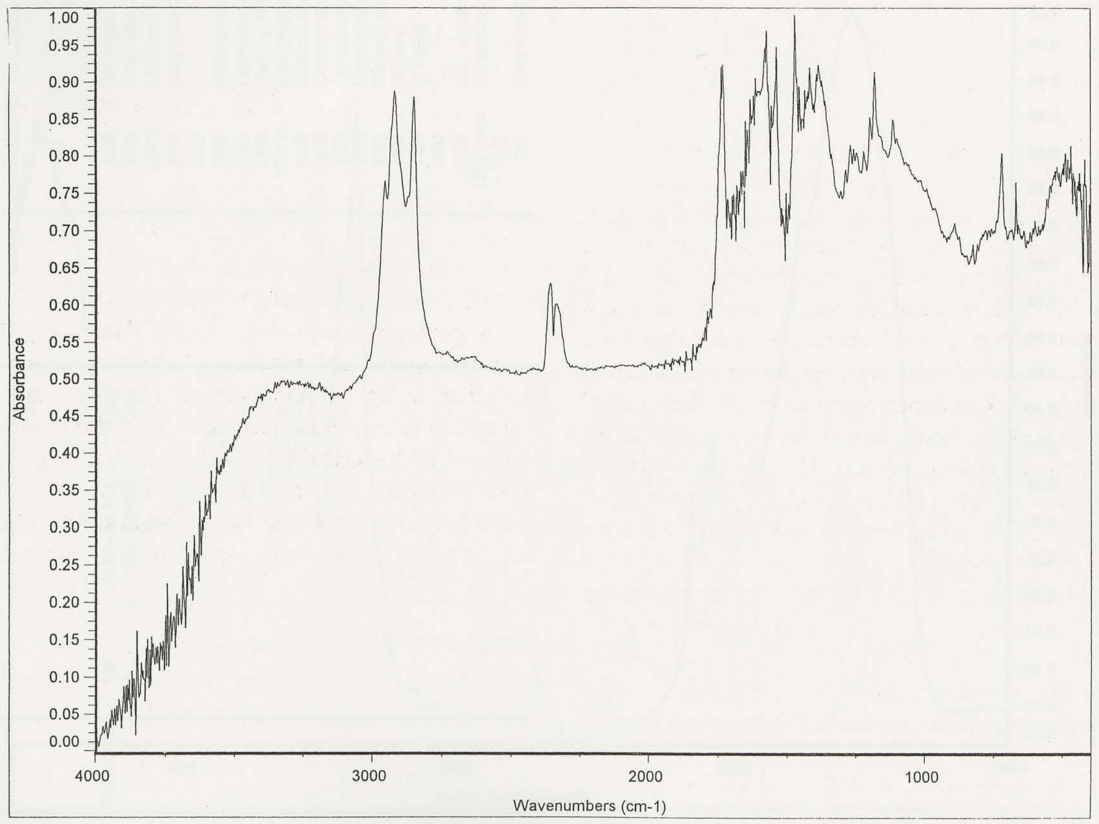

Figure 4 *Myrtos Phournou Koryphe (EUM 99): infrared spectrum*

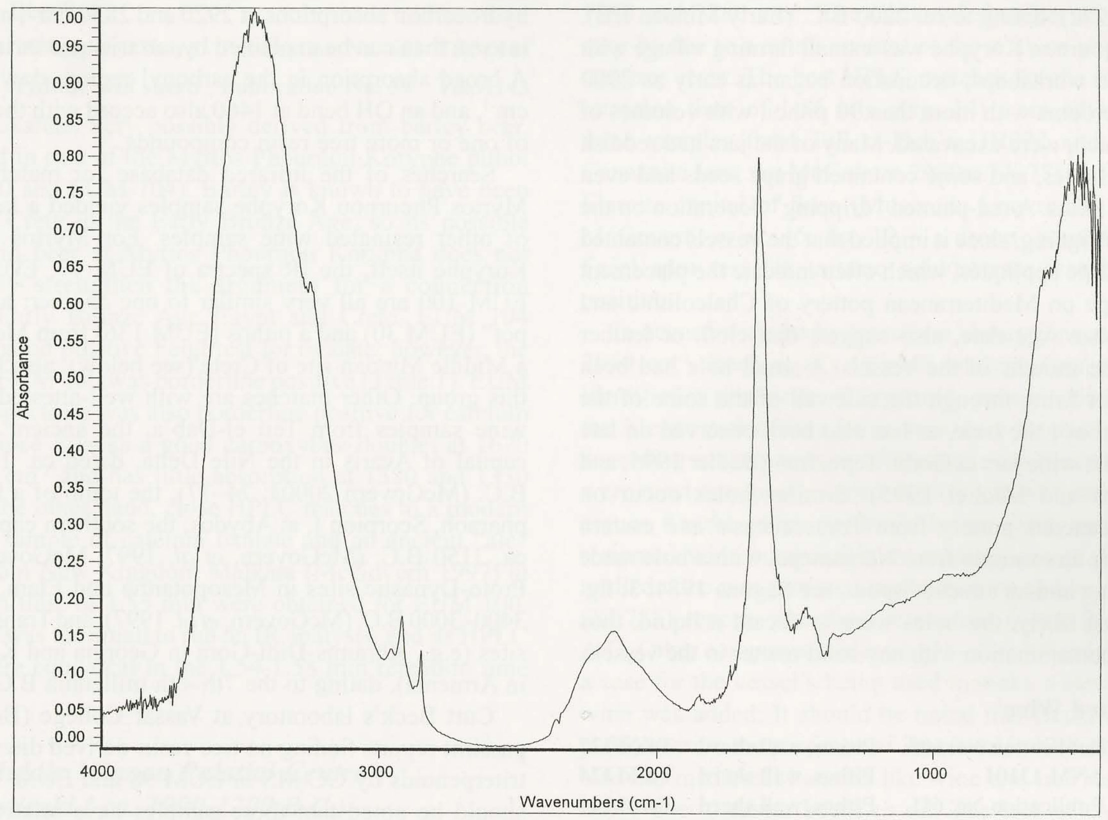

Figure 5 *Myrtos Phournou Koryphe (EUM 100): infrared spectrum*

3. Feigl Chemical Spot Tests

Two standard wet chemical tests, developed by Fritz Feigl (1966), provide corroborative evidence for tartaric acid/tartrate and oxalate. The sensitivity of the tests is on the order of a microgram. The presence of tartaric acid/tartrate, which occurs in large amounts in the Middle East only in grapes (and therefore in wine), was confirmed by dissolving and heating the ancient sample in concentrated sulfuric acid. β, β′-dinaphthol is then added, to convert tartaric acid to a compound that exhibits green fluorescence under ultraviolet light. The specific test for barley beer focuses on calcium oxalate, which is a principal component of "beerstone" which settles out at the bottom and along the sides of barley beer processing and storage vessels. The oxalate is reduced by zinc granules in an acidic medium to glyoxalic acid, followed by reaction with phenylhydrazine and hydrogen peroxide, to give a distinctive pinkish red color.

If the results from the three different chemical analyses reinforce one another, one can be relatively confident that the compounds have been identified. Still, since the ancient samples can represent complex mixtures of many different compounds, it is important to follow up this work with mass spectrometric analyses, whether starting with a gas chromatographic or liquid chromatographic separation. There is no guarantee that mass spectrometry will resolve all outstanding issues as to the identity of an organic compound. Indeed, in the case of low molecular weight acids and salts, the Feigl spot tests can be more informative than mass spectrometry, which identifies these compounds with difficulty.

In summary, the MASCA Molecular Archaeology Laboratory primarily relies on three complementary chemical techniques – DRIFTS, HPLC, and Feigl spot tests – to test an ancient organic sample for the presence of specific marker or fingerprint compounds. Large databases of relevant archaeological and modern reference samples are then searched for the closest chemical matches. The fingerprint compounds are then correlated to natural products and sources of historical and archaeological significance. To resolve discrepancies between the analyses and shed additional light on the ancient organics, follow-up LC-MS and GC-MS analyses are carried out at outside facilities.

II. Experimental Results

1. The Early Bronze Age settlement of Myrtos Phournou Koryphe (ca. 2200–B.C.)

The earliest pottery that was analyzed by the MASCA laboratory were large storage jars (pithoi) from the site of Myrtos Phournou Koryphe along the southern coast of Crete

(Warren 1972), dating to ca. 2200 B.C. (Early Minoan IIB). Myrtos Phournou Koryphe was a small farming village with houses and workshops; occupation began as early as 2900 B.C. Storerooms with more than 90 pithoi, with volumes of 90 litres each, were excavated. Many of the jars had reddish interior residues, and some contained grape seeds and even stems and skins. A red-painted "dripping" decoration on the jars was intriguing, since it implied that the vessels contained a liquid. Rope appliqués, which often indicate the placement of real rope on Mediterranean pottery of Chalcolithic and Early Bronze Age date, also suggest that cloth or leather covered the mouths of the vessels. A small hole had been drilled after firing through the sidewall of the some of the jars, just above the base, as has also been observed on late Chalcolithic wine jars at Godin Tepe, Iran (Badler 1995, and McGovern and Michel 1995). Similar holes occur on contemporaneous pottery from Transcaucasia and eastern Turkey (for an example from Norşuntepe, with a hole made before firing and an attached spout, see Sagona 1984: 3: fig. 89.3). Most likely, the holes were to decant a liquid, thus avoiding contamination with any solid matter in the vessels.

a. Resinated Wine[1]

EUM 95	**Publication No. 605**	**Pithos, wall sherd**	**T&M 127**
EUM 97	**ANM 13101**	**Pithos, wall sherd**	**T&M 124**
EUM 98	**Publication No. 611**	**Pithos, wall sherd**	**T&M 126**
EUM 99	**Publication No. 604**	**Pithos, wall sherd**	**T&M 125**
EUM 100	**Publication No. 623**	**Pithos, wall sherd**	**T&M 144**
EUM 104	**Publication No. 59**	**Pithos, wall sherd**	**T&M 143**

The six analyses of Myrtos Phournou Koryphe pithoi gave very similar DRIFTS, HPLC, and spot test results (see Table 1; note that EUM 104, however, was too small for IR analysis). Tartaric acid was well attested in the IR spectra (see Figs. 1–5) by a sharp, intense carbonyl peak at 1720/1740 cm^{-1}, together with other absorptions at 1440 and 1250 cm^{-1} in the so-called fingerprint region from about 1550 to 800 cm^{-1}. Tartrate, which was probably present as either the potassium or calcium salts, had carboxylate absorptions at maxima of 1630 and 1560 cm^{-1} with additional peaks at 1550, 1480, 1380, 1330, 1270, 600, 560, and 480 cm^{-1}. The presence of tartaric acid/tartrate was borne out by all the samples testing positive for the Feigl spot test. The HPLC search results of the fraction coming off at retention times between 1.54 and 1.58 min bore out this finding (Figs. 6–11): the closest matches were with resinated wine samples (e.g., Hajji Firuz Tepe, the earliest chemically identified wine residue thus far published – see McGovern, *et al.* 1996 and 1997). A tree resin was also indicated by close matches with pine and terebinth tree resin at retention times as high as 1.63 min. (Fig. 11), and is consistent with the strong hydrocarbon absorptions at 2920 and 2850 cm^{-1}, much more intense than can be explained by tartaric acid/tartrate alone. A broad absorption in the carbonyl region, down to 1695 cm^{-1}, and an OH bend at 1460 also accord with the presence of one or more tree resin compounds.

Searches of the infrared database for matches to the Myrtos Phournou Koryphe samples yielded a large group of other resinated wine samples. For Myrtos Phournou Koryphe itself, the IR spectra of EUM 97, EUM 98 and EUM 100 are all very similar to one another; a "cooking pot" (EUM 30) and a pithos (EUM 136) from Monastiraki, a Middle Minoan site of Crete (see below), also belongs to this group. Other matches are with well-attested resinated wine samples from Tell el-Dab`a, the ancient "Hyksos" capital of Avaris in the Nile Delta, dated ca. 1900–1550 B.C. (McGovern 2000a: 74–77); the tomb of a Dynasty 0 pharaoh, Scorpion I, at Abydos, the southern capital, dated ca. 3150 B.C. (McGovern, *et al.* 1997, McGovern 1998); Proto-Dynastic sites in Mesopotamia and Elam, dated ca. 3400–3000 B.C. (McGovern, *et al.* 1997); and Transcaucasian sites (e.g., Khramis-Didi-Gora in Georgia and Khatunarkh in Armenia), dating to the 7th–6th millennia B.C.

Curt Beck's laboratory at Vassar College (Beck *et al.*, passim) reports finding no tree-resin-derived diterpenoid or triterpenoids by GC-MS in EUM 98 and EUM 100, but it should be noted that these samples have relatively small hydrocarbon peaks compared to the other Myrtos Phournou Koryphe samples and thus the concentration of tree resin would be less and not as easily detectible. EUM 100 also appears to have been used for barley beer (below).

Tartaric acid or a tartrate salt is characteristic of a grape product, because these compounds occur naturally in the Mediterranean-Near Eastern region only in grape (*Vitis vinifera*). Outside of the Middle East and Europe, it is also found in the African baobab tree and the fruit of the South Asian tamarind tree, but it highly unlikely that products of these trees were traded during the Bronze Age. The insoluble potassium bitartate and calcium tartrate salts are readily formed from the acid, and in unfiltered, unrefined wine, a crystalline accumulation of these salts, the so-called dregs or lees, will sometimes form on the bottom of a wine vessel. Expressed as the liquid, grape juice quickly ferments in a non-oxygen or anaerobic environment to alcohol, especially given the slow pressing methods in antiquity and the high temperatures of the Middle East. The microscopic culprit responsible for the transformation is the natural yeast on the surface bloom of some grape skins, *Saccharomyces cerevisiae.* Recently, a precursor of this yeast has been identified by DNA analysis inside the Scorpion I wine jars at Abydos, dated to ca. 3150 B.C. (Cavalieri, *et al.* 2003).

[1] Editor's note: In the Project, *Archaeology Meets Science,* a distinction is made between wine made with tree resin, and retsina as defined in modern Greece, a pine-resinated wine. It should be noted however that some modern Greek resinated wine is made with North African sandarac resin.

b. Barley Beer?

EUM 100	**Pithos, wall sherd**	**Publication No. 623**	**T&M144**
EUM 104	**Pithos, wall sherd**	**Publication No. 59**	**T&M143**

Calcium oxalate, very possibly derived from barley beer, was found in two of the Myrtos Phournou Koryphe pithoi (EUM 100 and EUM 104). Barley is known to have been grown in Crete in the Early Bronze Age, so its possible presence in beer at Myrtos Phournou Koryphe does not necessarily strengthen the argument for a connection between Early Bronze Age Egypt and Crete. EUM 104 yielded a good positive Feigl test for oxalate; however, the result for EUM 100 was borderline positive (Table 1). EUM 100's IR spectrum was also borderline positive for calcium oxalate, since it lacks a good carboxylate doublet at 1670 and 1605 cm^{-1} and has little absorption at 1380 and 1330 cm^{-1}. On the other hand, close HPLC matches to a modern reference sample of calcium oxalate and an ancient "ale" sample from New Kingdom Malkata (McGovern 1997) at a retention time of 1.55 min were obtained for EUM 100. EUM 104 was too small to run an IR analysis, and its HPLC results were equivocal in the 1.54-1.58 min retention time range.

2. *The Middle Minoan Palatial Centre at Monastiraki (ca. 1900-1700 B.C.)*

The next result that indicated the presence of ancient resinated wine in Greece, according to the EUM analyses, came some 500 years later at Monastiraki, ca. 1700 B.C. The site, excavated by Athanasia Kanta is a small Middle Minoan IIB palatial centre, located along the main north-south road through the Amari valley, which was probably influenced, if not controlled by, Phaistos in the Protopalatial period. Over 100 pithoi of remarkably similar type to those at Myrtos Phournou Koryphe with red-painted trickle patterns running down their bodies and upper and lower handles were recovered from some 80 storerooms (the number is an estimate by the excavator). The main stylistic difference of the Monastiraki jars in comparison with the Myrtos Phournou Koryphe pithoi was that they lacked rope decoration.

EUM 30 Tripod cooking pot, base/leg sherd T&M 128

A sherd from a tripod cooking pot (EUM 30) would appear to be an unlikely candidate for finding any ancient organic evidence, let alone a grape product such as wine, since it would be expected that if it were used for cooking, the organics would have been degraded or destroyed. But, our chemical evidence, as well as that of Curt Beck's laboratory (this volume), show unequivocally that a grape product was present in the vessel. The infrared spectrum (Fig. 12) has a broad absorption band in the region from 1630 to 1560 cm^{-1}, which accords with tartrate, as do the peaks at 1380 and 1280 cm^{-1}. The carbonyl shoulder at 1720 cm^{-1} may be due to a small amount of the acid, or alternatively, to a tree resin. The best HPLC matches for the sample at a retention time of 1.56 min (Fig. 14) were with resinated wine samples from Tell el-Dab`a (JH082 and 7648M – Canaanite Jars; see McGovern 2000a: 74–77) and the proto-Elamite capital of Susa (Musée du Louvre Sb18869; see McGovern, *et al.* 15, fig. 12 – a droop-spouted jar). The Feigl spot test for tartaric acid/tartrate was borderline positive.

In accord with the hydrocarbon absorptions at 2920 and 2850 cm^{-1}, Beck et al's GC-MS analysis (see pp. 33–36) identified a pine resin diterpenoid, possibly derived from the Aleppo pine (*Pinus halepensis*) (see footnote on p. 29), according to the presence of benzoic acid. Since tree resins were most commonly added to wine (above), this evidence argues for the grape product's being wine, specifically a resinated wine comparable to modern *retsina*. Perhaps, a mulled wine was prepared in the cooking pot, as Atheneaus (XI.783) reports that the Cretans did in the 2nd century A.D. Other components identified by GC-MS might support a case for the vessel's being used to make a stew to which wine was added. It should be noted that Beck, *et al.* (see p. 35) ascribe the presence of 2-octanol, which intriguingly also has medicinal benefits like wine and tree resins, most likely due to castor beans or oil. The lack of carbon soot from firing on the exterior of the "cooking pot" might suggest that the vessel may have been a container for wine, pure and simple, but only a sherd survived.

Another very curious component associated with the resinated wine in this vessel was identified by Beck, *et al.* (see p. 34): an alkyl-γ-lactone, most likely 3-methyl-4-nonanolide. It is derived principally from oak wood/resin, and is referred to as whiskey or cognac lactone because the distinctive flavor and aroma of this compound is imparted to Irish whisky and French cognac by ageing in oak barrels or adding oak chips. The concentration of this lactone is enhanced if the oak wood has been toasted, as is done in bending the staves of barrels.

EUM 136 Pithos, wall sherd Publication No. 8 T&M 129

The other sample from Monastiraki (EUM 136) came from a pithos, one of numerous examples from the storerooms. Its IR spectrum (Fig. 13) has clear absorption bands for tartaric acid, tartrate, and a probable tree resin. The LC search at a retention time of 1.59 min (Fig. 15) produced a good match with an early New Kingdom plaster grape-treading installation at Tell el-Dab`a (see above). The Feigl spot test for tartaric acid/tartrate was borderline positive. Like the pithoi found in storerooms at the Early Minoan site of Myrtos Phournou Koryphe, resinated wine appears to have been produced and stored in similar fashion at Middle Minoan Monastiraki.

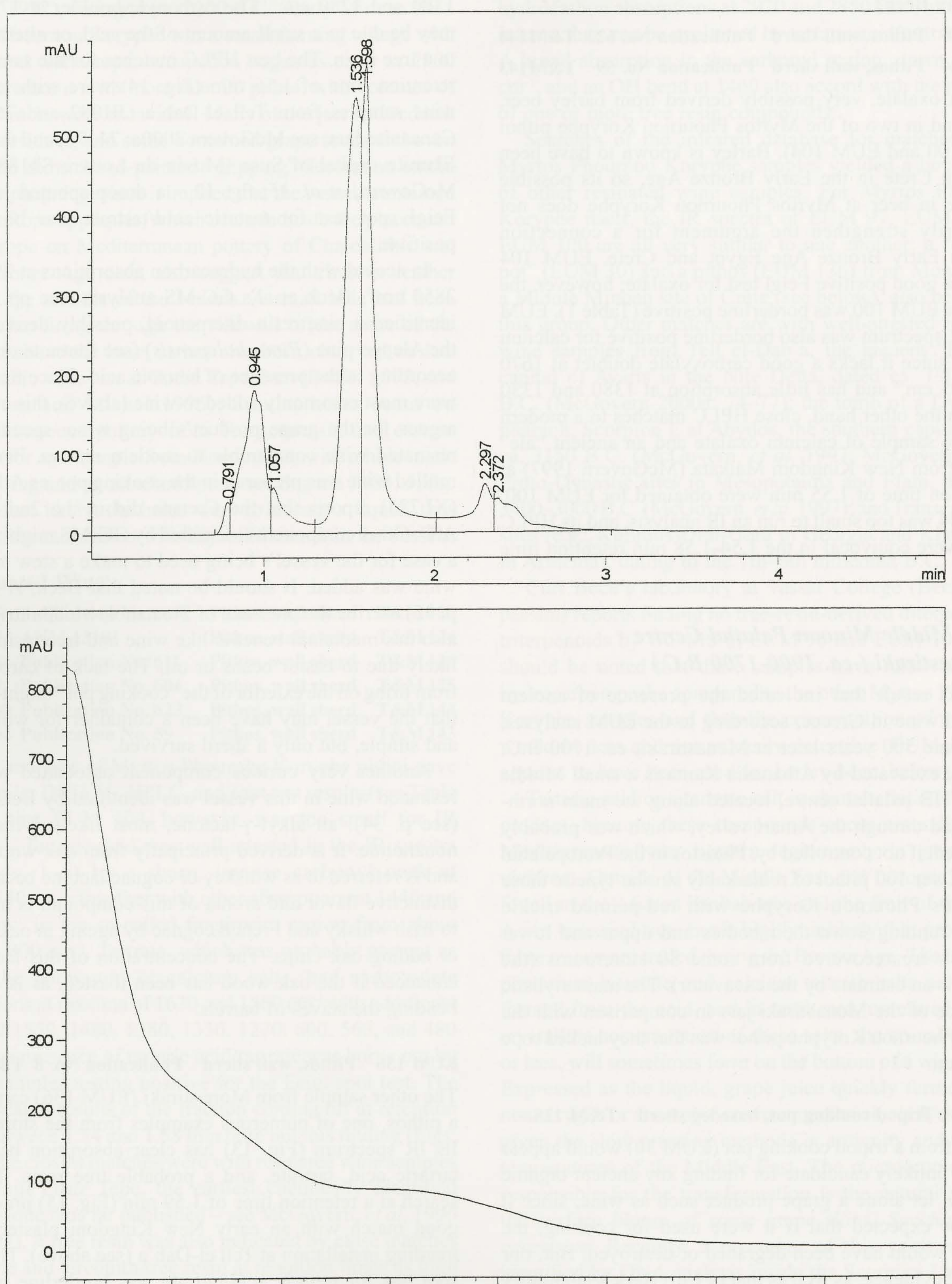

Figure 6 *Myrtos Phournou Koryphe (EUM 95): liquid chromatogram and UV absorption spectrum at 1.54 min*

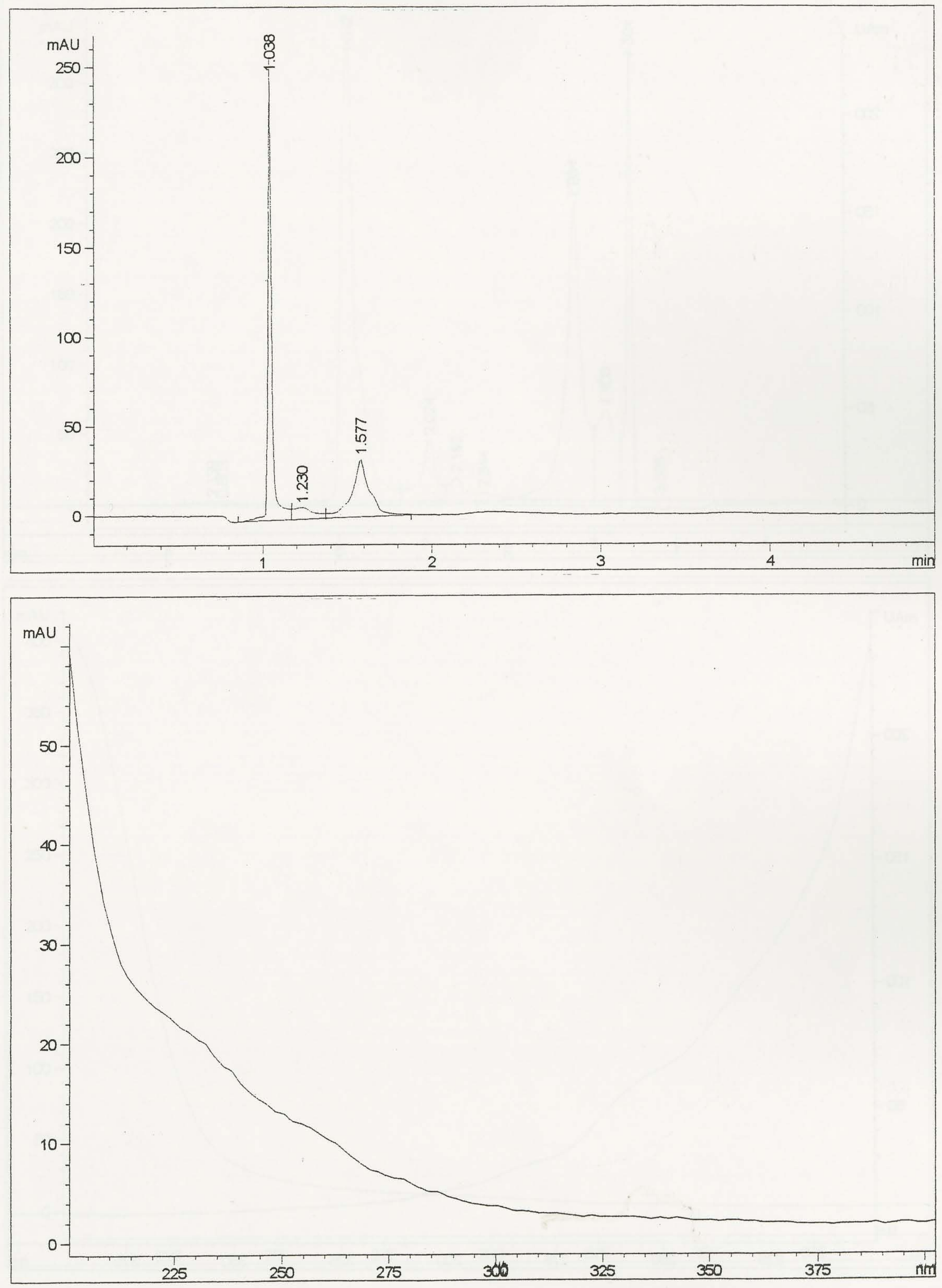

Figure 7 *Myrtos Phournou Koryphe (EUM 97): liquid chromatogram and UV absorption spectrum at 1.58 min*

Figure 8 Myrtos Phournou Koryphe (EUM 98): liquid chromatogram and UV absorption spectrum at 1.59 min

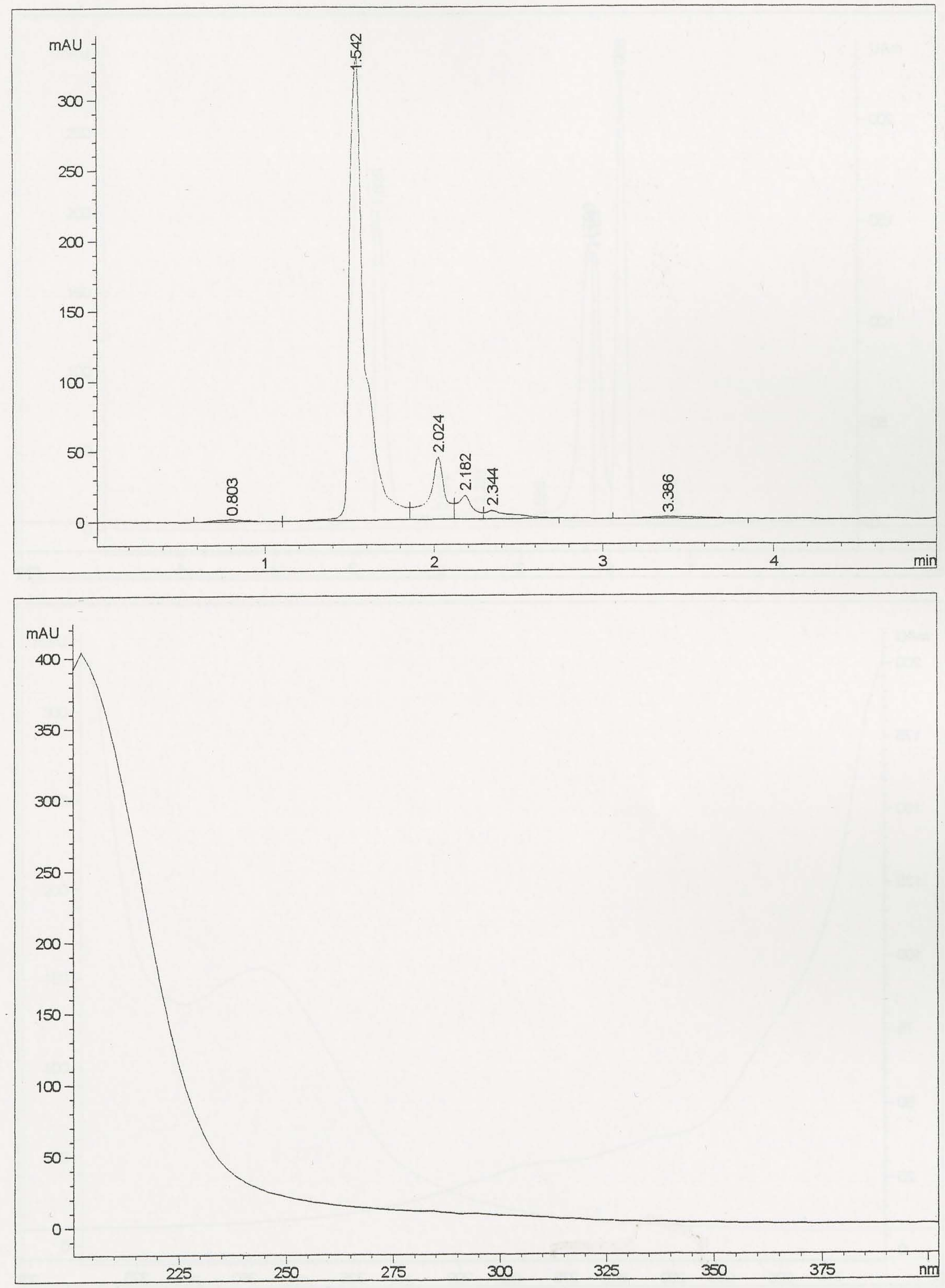

Figure 9 Myrtos Phournou Koryphe (EUM 99): liquid chromatogram and UV absorption spectrum at 1.54 min

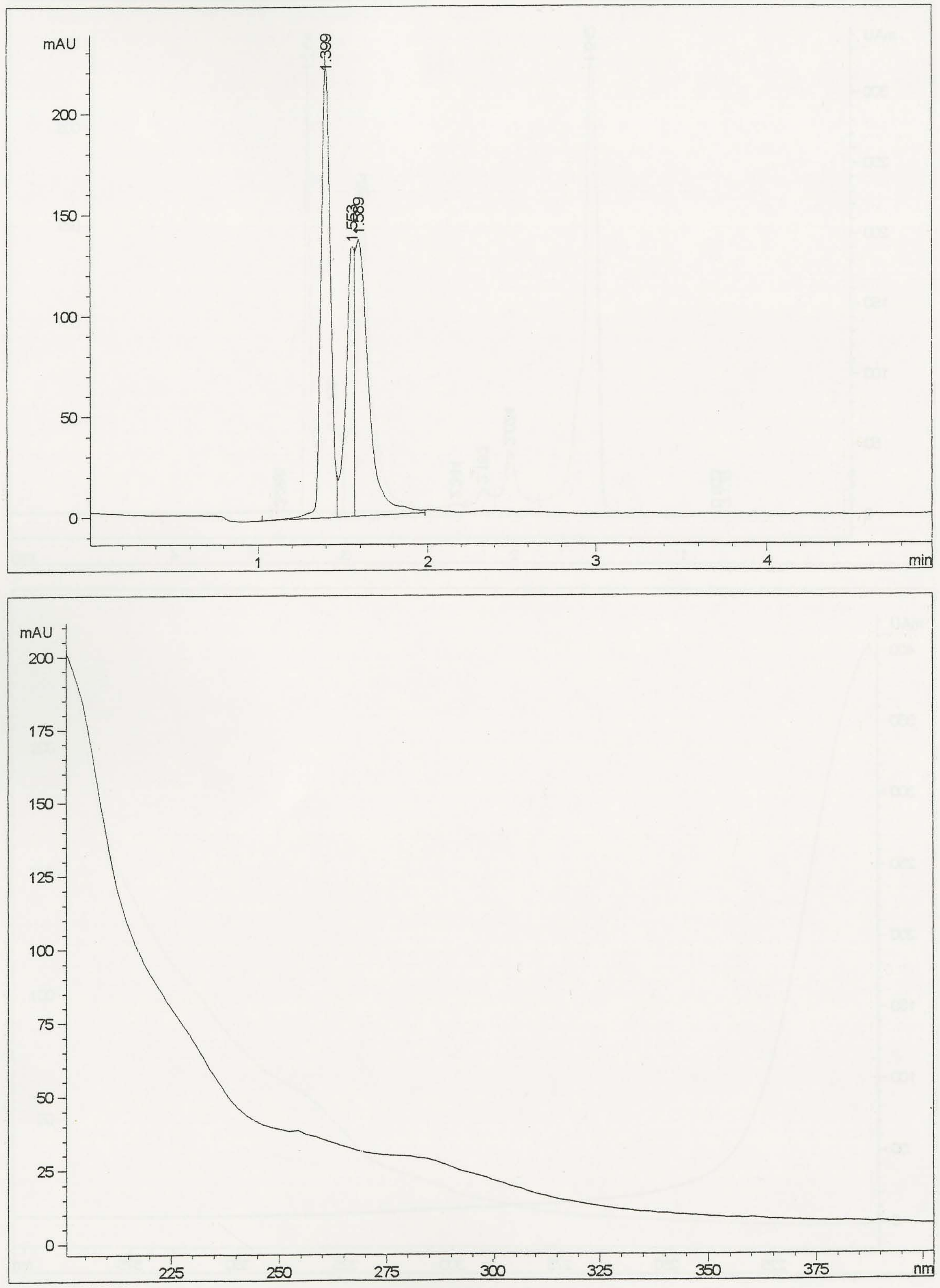

Figure 10 *Myrtos Phournou Koryphe (EUM 100): liquid chromatogram and UV absorption spectrum at 1.55 min*

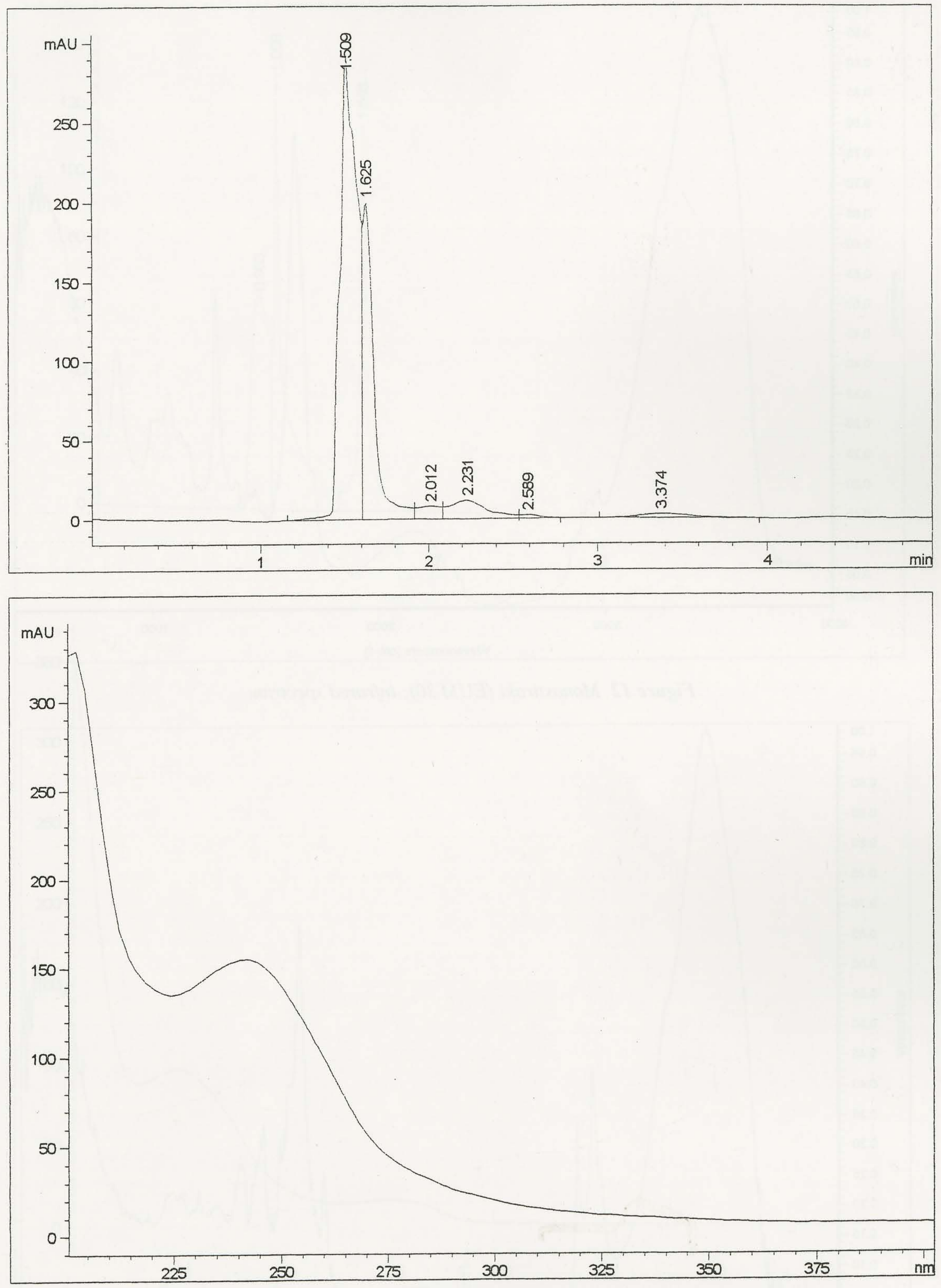

Figure 11 *Myrtos Phournou Koryphe (EUM 104): liquid chromatogram and UV absorption spectrum at 1.63 min*

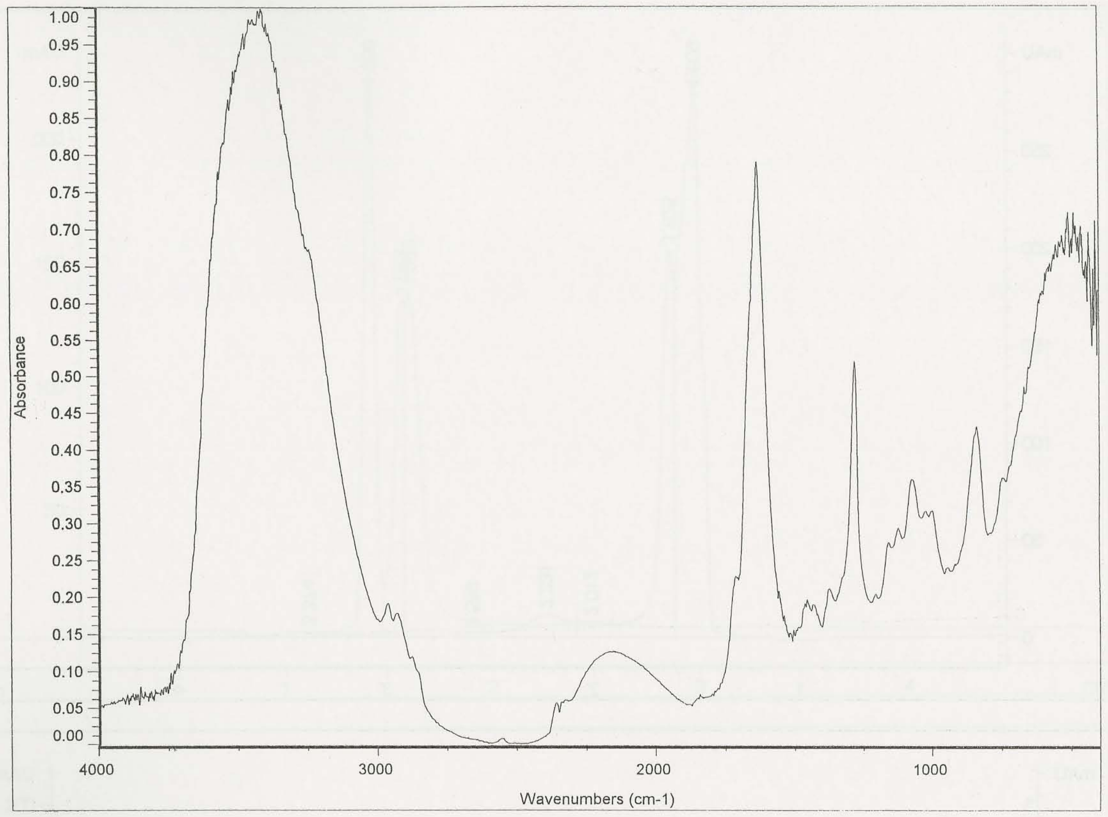

Figure 12 *Monastiraki (EUM 30): infrared spectrum*

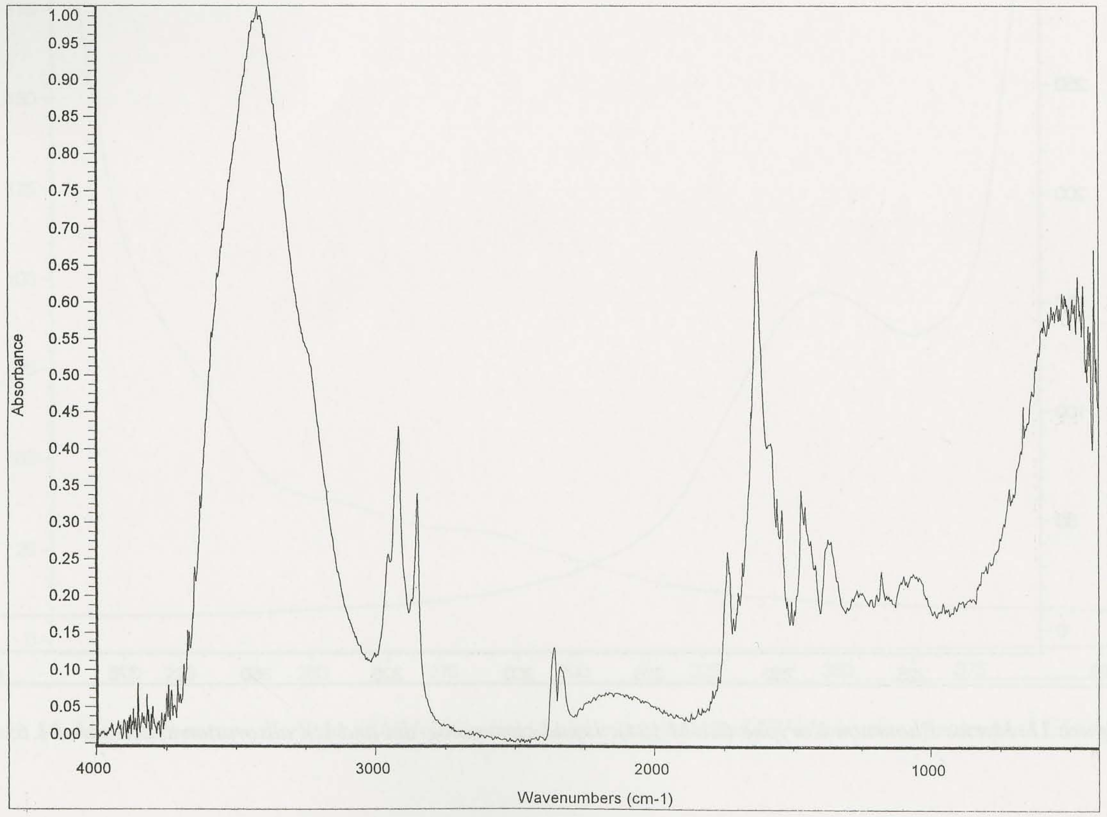

Figure 13 *Monastiraki (EUM 136): infrared spectrum*

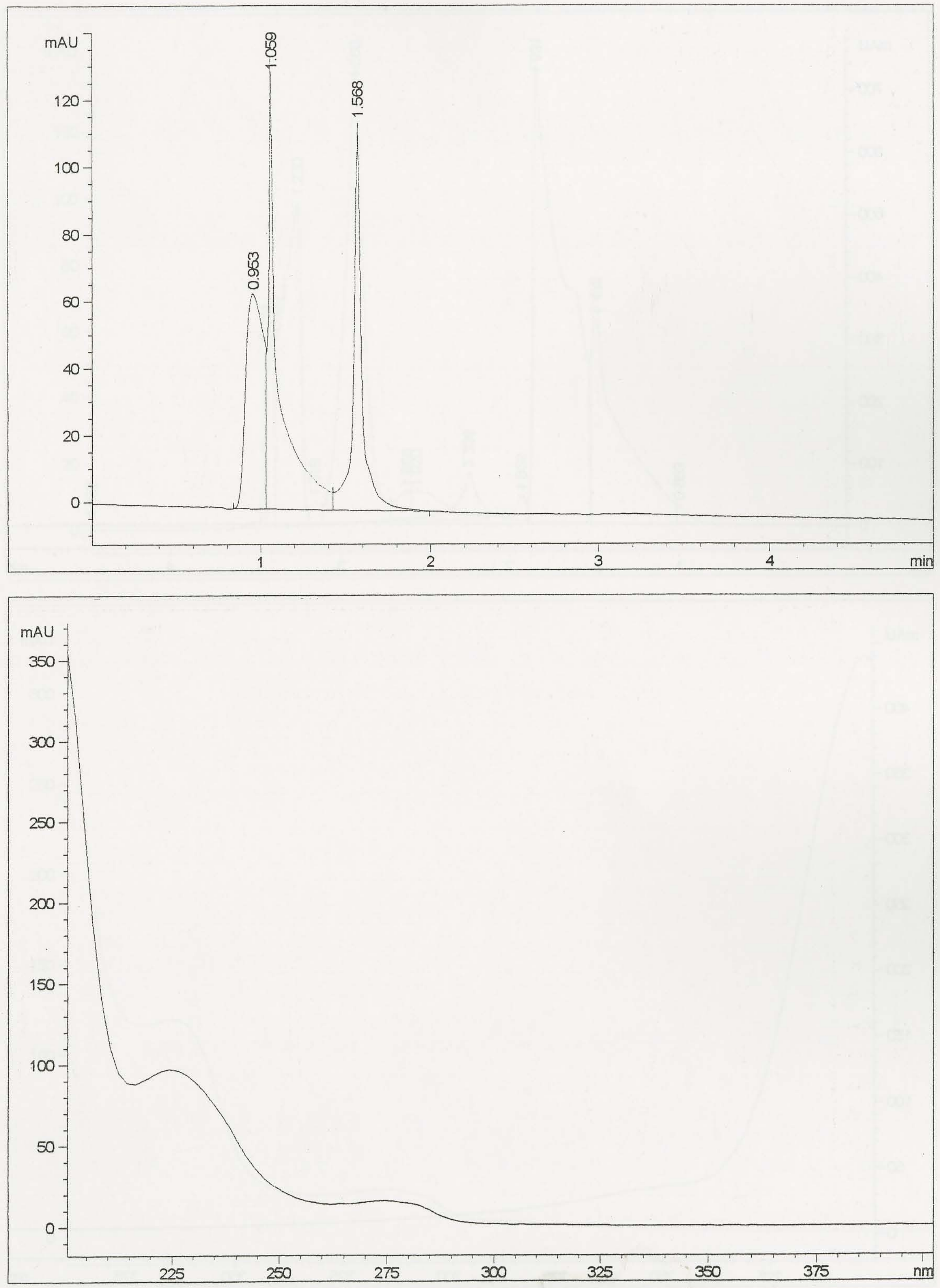

Figure 14 *Monastiraki (EUM 30): liquid chromatogram and UV absorption spectrum at 1.56 min*

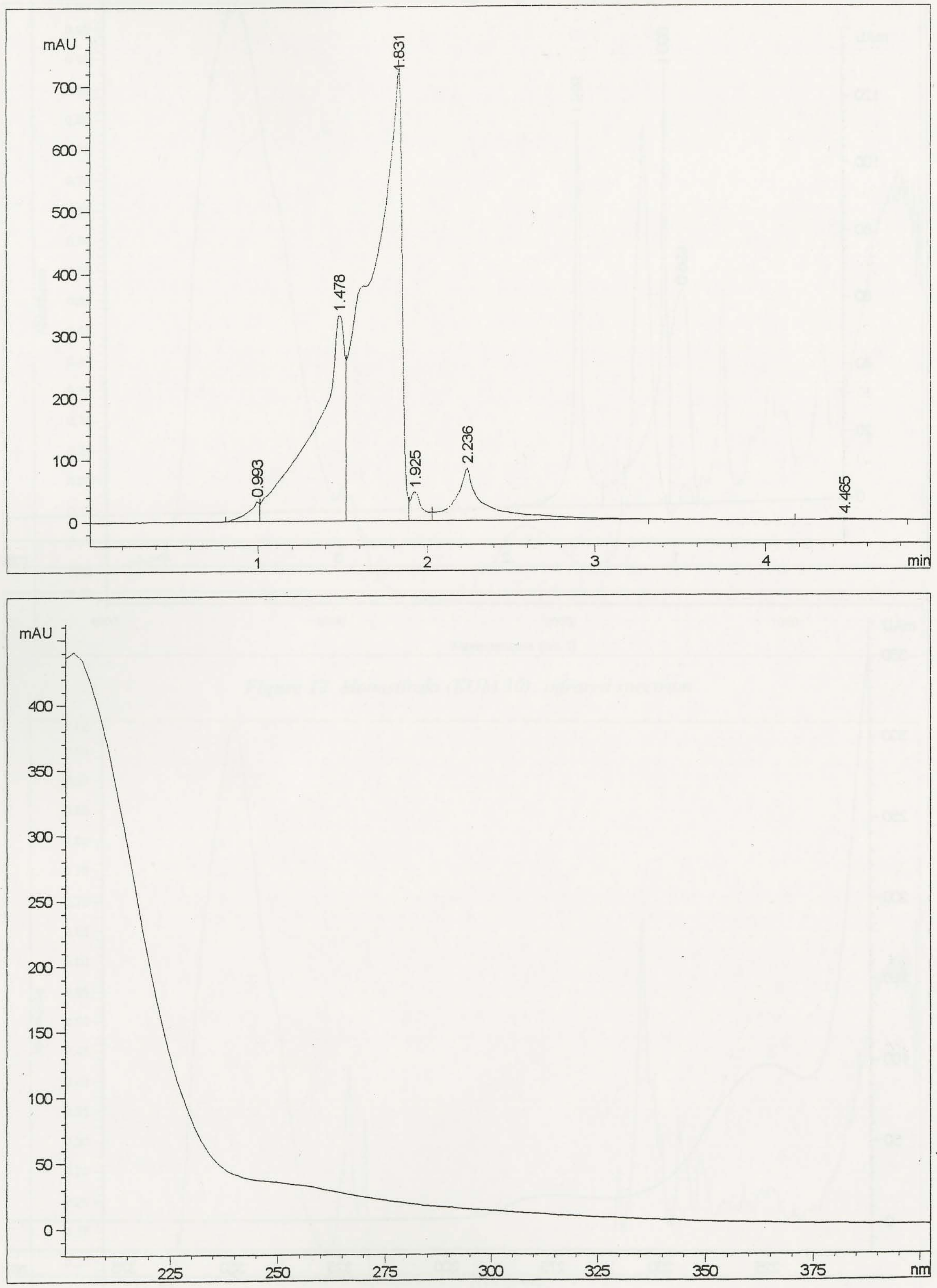

Figure 15 *Monastiraki (EUM 136): liquid chromatogram and UV absorption spectrum at 1.58 min*

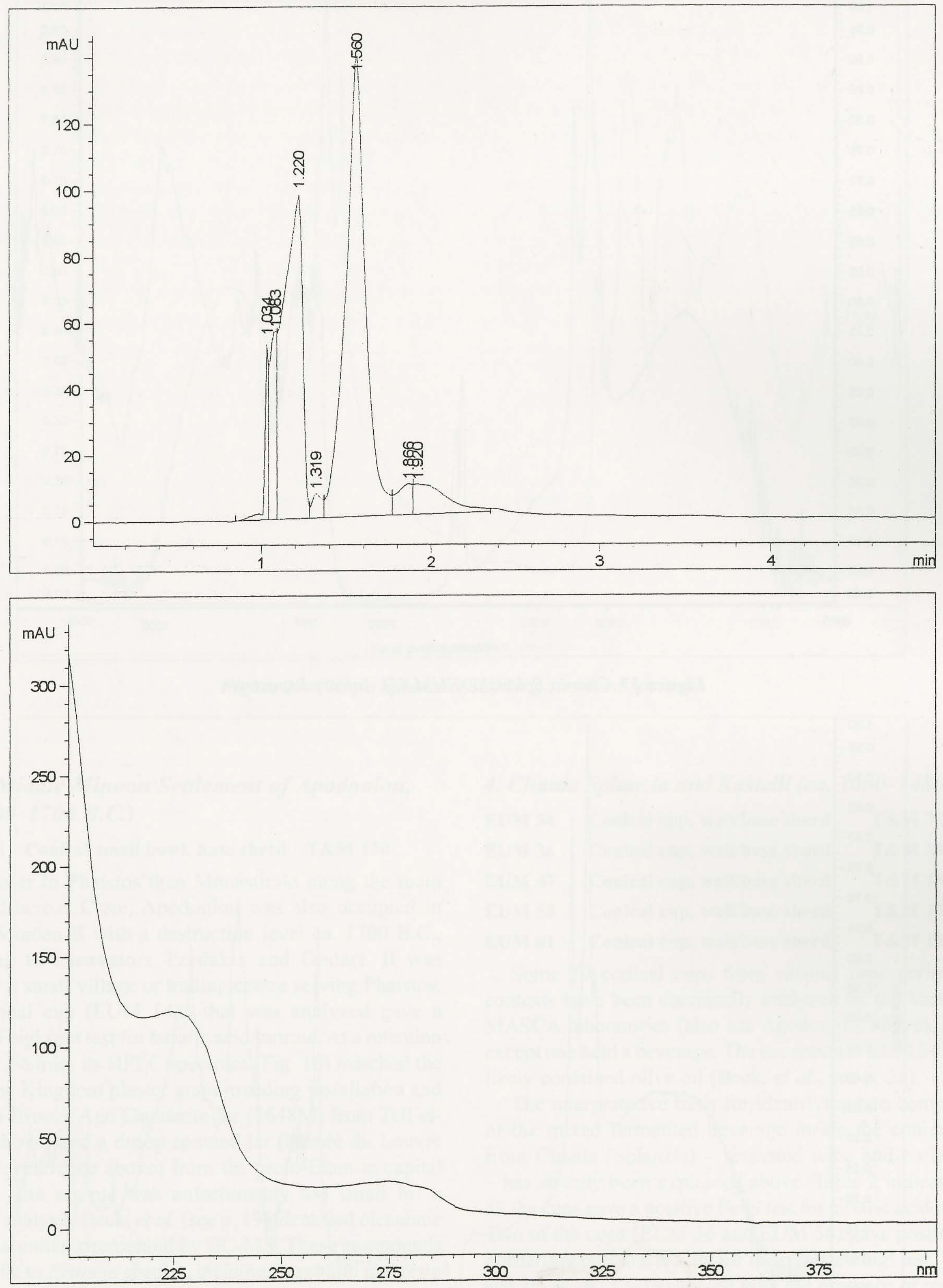

Figure 16 *Apodoulou (EUM 148): liquid chromatogram and UV absorption spectrum at 1.56 min*

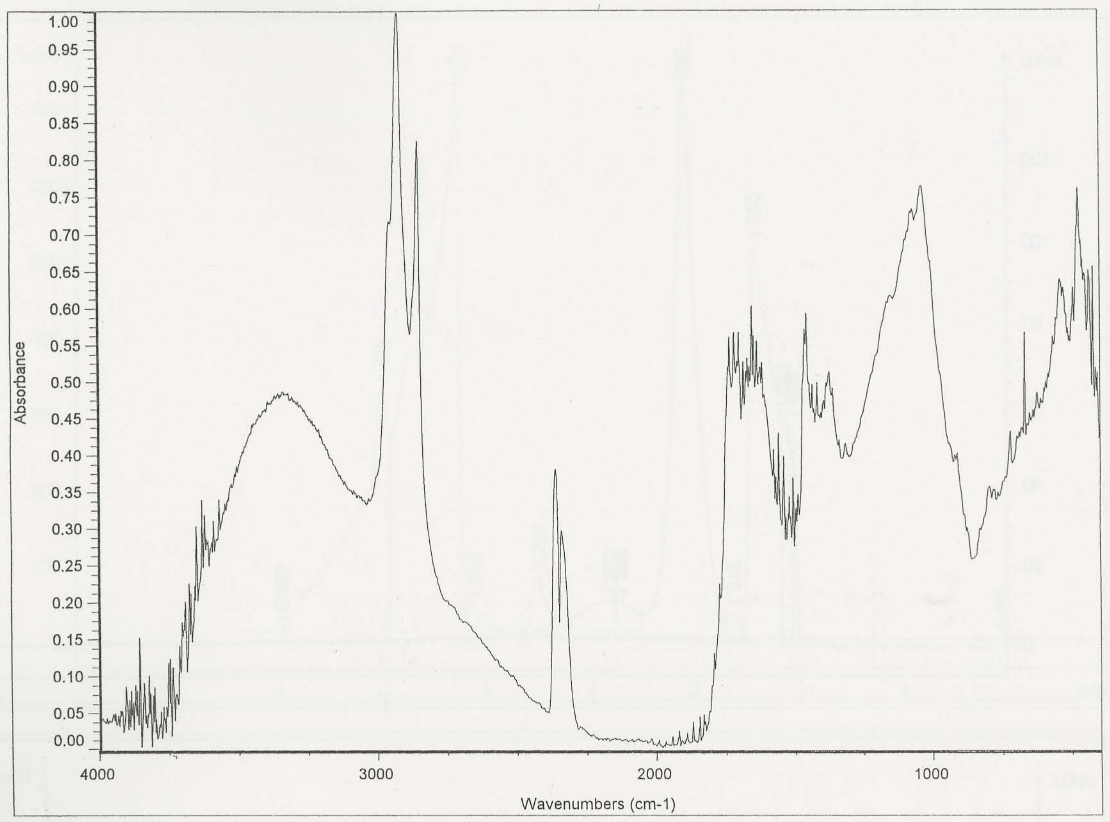

Figure 17 *Chania Splanzia (EUM 47): infrared spectrum*

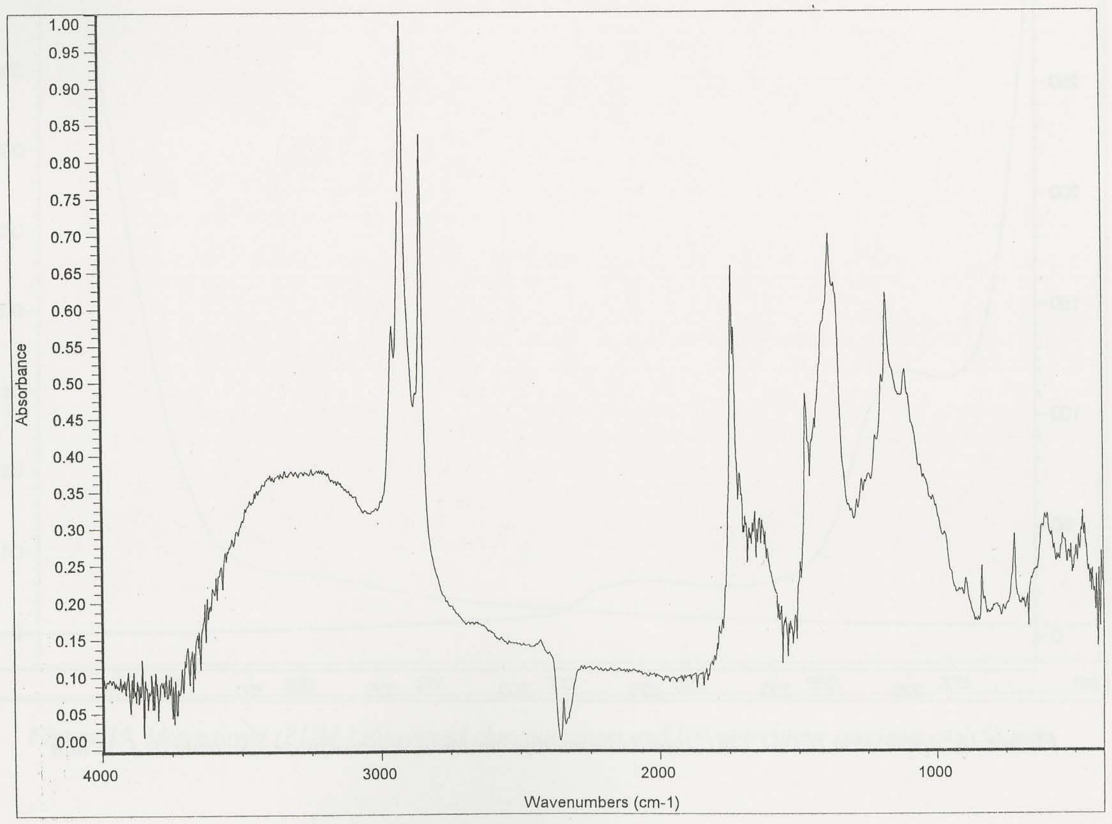

Figure 18 *Chania Splanzia (EUM 58): infrared spectrum*

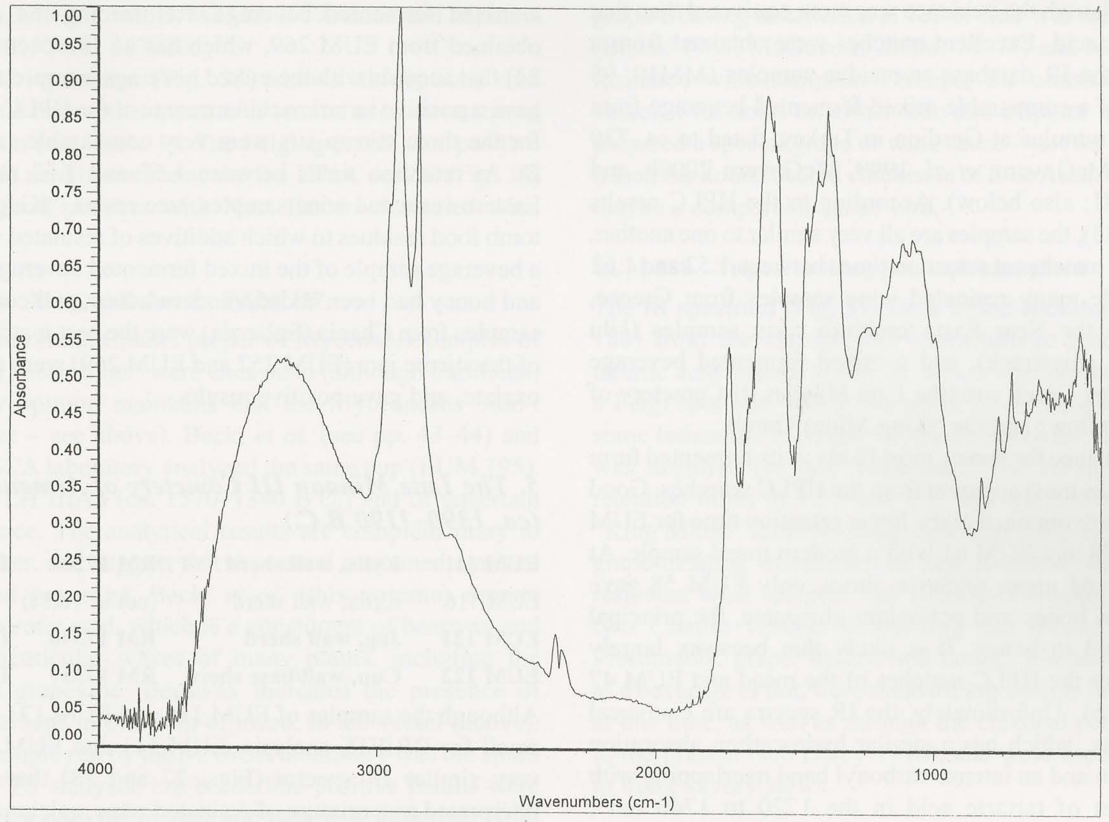

Figure 19 *Chania Splanzia (EUM 61): infrared spectrum*

3. The Middle Minoan Settlement of Apodoulou, (ca. 1900–1700 B.C.)

EUM 148 Conical small bowl, base sherd T&M 130

Lying closer to Phaistos than Monastiraki along the main N-S road across Crete, Apodoulou was also occupied in Middle Minoan II with a destruction level ca. 1700 B.C., according to excavators Tzedakis and Godart. It was probably a small village or trading centre serving Phaistos. The conical cup (EUM 148) that was analyzed gave a positive Feigl spot test for tartaric acid/tartrate. At a retention time of 1.56 min, its HPLC spectrum (Fig. 16) matched the early New Kingdom plaster grape-treading installation and a Middle Bronze Age Canaanite Jar (7648M) from Tell el-Dab`a (above) and a droop-spouted jar (Musée du Louvre Sb18869; reference above) from the proto-Elamite capital of Susa. The sample was unfortunately too small for a DRIFTS analysis. Beck, *et al.* (see p. 19) identified oleanonic acid and another triterpenoid by GC-MS. These compounds are specific to *Pistacia* species, including terebinth tree resin (*Pistacia atlantica* Desf.).

4. Chania Splanzia and Kastelli (ca. 1600–1480 B.C.)

EUM 34	**Conical cup, wall/base sherd**	**T&M 76**
EUM 36	**Conical cup, wall/base sherd**	**T&M 133**
EUM 47	**Conical cup, wall/base sherd**	**T&M 154**
EUM 58	**Conical cup, wall/base sherd**	**T&M 156**
EUM 61	**Conical cup, wall/base sherd**	**T&M 155**

Some 20 conical cups from various time periods and contexts have been chemically analyzed by the Vassar and MASCA laboratories (also see Apodoulou, above), and all except one held a beverage. The exception is EUM 34, which likely contained olive oil (Beck, *et al.*, see p. 28).

The interpretative basis for identifying two components of the mixed fermented beverage inside the conical cups from Chania (Splanzia) – resinated wine and barley beer – has already been explained above. Table 2 indicates that all the cups gave a positive Feigl test for tartaric acid/tartrate. Two of the cups (EUM 36 and EUM 58) gave positive and borderline positive results for the oxalate Feigl test. The IR spectra (Figs. 17–19) accord with the presence of resinated wine in all the samples, except EUM 36 which was too small to analyze. Tartrate and calcium oxalate, possibly deriving from barley beer, were also indicated in the IR spectra, although the evidence was more equivocal than that for tartaric acid. Excellent matches were obtained from a search of the IR database to residue samples (MM10, 95 and 128) of a comparable mixed fermented beverage from the Midas tumulus at Gordion in Turkey, dated to ca. 730 B.C. (see McGovern, *et al.* 1999, McGovern 2000b, and Young 1981; also below). According to the HPLC results (Figs. 20–23), the samples are all very similar to one another. Additional matches at retention times between 1.52 and 1.62 min include many resinated wine samples from Greece, Egypt and the Near East, terebinth resin samples (Ulu Burun/Kaş shipwreck), and a mixed fermented beverage from another Greek site (the Late Minoan III Cemetery of Armenoi, below) and the "King Midas" tomb.

The evidence for honey, most likely in its fermented form as mead, was most apparent from the HPLC searches. Good matches were obtained at the lower retention time for EUM 47, EUM 58 and EUM 61 with a modern mead sample. At the lower and upper retention times, only EUM 58 gave evidence of honey and potassium gluconate, the principal organic acid in honey. It is likely that beeswax largely accounts for the HPLC matches of the mead and EUM 47 and EUM 61. Unfortunately, the IR spectra are equivocal for beeswax, which has a similar hydrocarbon absorption as tree resin and an intense carbonyl band overlapping with the doublet of tartaric acid in the 1720 to 1740 cm^{-1}; additional absorptions in the "finger-print" region (e.g., at 1460 and 1170 cm^{-1}) are also equivocal.

The HPLC evidence, however, makes it clear that the mixed beverage also included honey, one of the few natural sources of simple sugars in antiquity. This marvelously delicious and fragrant natural product is made only by a range of bee species found in temperate climates around the world (the European honey bee, *Apis mellifera,* being the best known). Although the sugars in honey rapidly degrade, another product of bees – beeswax – is virtually impossible to filter out completely when processing honey and its long hydrocarbons and related acids and esters can be very well preserved (Evershed 1997). When diluted down to 30% honey and 70% water, osmophilic yeasts in the honey will start the fermentation, and produce mead.

EUM 252	**Stirrup jar, wall sherd**	**T&M 166**
EUM 267	Stirrup jar, wall sherd	(not in T&M)
EUM 269	**Stirrup jar, wall sherd**	**T&M 165**

Three stirrup jars, representing fine (one marked with Linear B signs) and coarse types, were analyzed from the excavations at the Kastelli hill and its environs at Chania, carried out by Tzedakis and Andreadaki-Vlazaki. A palace complex of Late Minoan IA and later was revealed here in the old town. Although the samples of EUM 252 and EUM 267 were too small for DRIFTS analysis and gave negative tartaric acid/tartrate tests, their HPLC results (Figs. 25 and 26) best fit a mixed fermented beverage. Reinforcing the evidence obtained from EUM 269, which has an IR spectrum (Fig. 24) that accords with the mixed beverage interpretation and gave a positive tartaric acid/tartrate test, the HPLC searches for the three stirrup jars were very comparable (see Table 2). At retention times between 1.57 and 1.63 min, Near Eastern resinated wine samples, tree resins, "King Midas" tomb food residues to which additives of resinated wine and a beverage sample of the mixed fermented beverage, barley and honey had been added, modern honey, and conical cup samples from Chania (Splanzia) were the best matches. Two of the stirrup jars (EUM 252 and EUM 269) were tested for oxalate, and gave positive results.

5. The Late Minoan III Cemetery of Armenoi (ca. 1390–1190 B.C.)

EUM 111	**Kylix, wall sherd**	**RM 17284**	**T&M 167**
EUM 116	Kylix, wall sherd	(not in T&M)	
EUM 121	**Jug, wall sherd**	**RM 17340**	**T&M 168**
EUM 122	**Cup, wall/base sherd**	**RM 17337**	**T&M 169**

Although the samples of EUM 116 and EUM 121 were too small for DRIFTS analysis, EUM 111 and EUM 122 had very similar IR spectra (Figs. 27 and 28) that are best interpreted as a mixture of resinated wine, calcium oxalate, and beeswax components (Table 2). The HPLC results (Figs. 29–32) yielded good matches with mixed fermented beverage samples from the "King Midas" tomb, ancient Egyptian and Near Eastern resinated wine samples, modern potassium gluconate (a marker compound for honey), and two Greek samples from Chania and Chamalevri in the corpus. All the samples tested positive for the Feigl tartaric acid/tartrate test, except EUM 116; the oxalate test gave a positive for EUM 122 and a negative for EUM 116. Small sample size may possibly explain these discrepancies.

6. The Late Helladic Palace of Mycenae (ca. 1340–1250 B.C.)

EUM 67 Amphora/Canaanite jar, wall sherd Excavation no. 64-207;66-518 T&M 140

Like the amphoras (Canaanite jars) recovered from the Ulu Burun shipwreck (below), resinated wine was confirmed inside a comparable amphora type (EUM 67) from the Room with the Fresco in the Cult Centre (area 36) at the Citadel of Mycenae on Mainland Greece (Taylour 1983: fig. 23 and accompanying text), dating to Late Helladic IIIB1, ca. 1340–1250 B.C. (see also Beck, p. 36). This room clearly had a ceremonial function, with its altar, numerous vessels associated with food and drink, special objects (including ivory and Egyptian faience), and a back storeroom called "The Shrine" (see discussions by H. Martlew, E. B. French, O. Krzyszkowska, and D. Wardle in Tzedakis and Martlew 1999: 156–57 and 187–205).

The IR spectrum (Fig. 33) shows absorptions that correspond best with a mixture of tartaric acid, tartrate, and a tree resin (see Table 1). The Feigl spot test was positive for tartaric acid/tartrate test, and the HPLC results (Fig. 34) yielded good matches with Near Eastern resinated wine samples.

EUM 195 Mug, wall sherd T&M 157

Elsewhere on the Citadel proper of Mycenae, examples of so-called "beer mugs" were excavated (although traditional scholarly opinion maintains that the Mycenaeans didn't drink beer – see above). Beck, *et al.* (see pp. 43–44) and the MASCA laboratory analyzed the same cup (EUM 195), dated to LH IIIA2 (ca. 1370–1340 B.C.) and of uncertain provenience. The analytical results are complementary to one another, and suggest that the vessel contained a mixed fermented beverage. Beck, *et al.* (this volume) reports finding cerotic acid, which is a constituent of beeswax and other epicuticular waxes of many plants, including the Eurasian grapevine. Beeswax indicates the presence of honey, perhaps in the form of mead, in the vessel (above).

The sample run by the MASCA laboratory was too small for DRIFTS analysis, but borderline positive results were obtained for both the oxalate and tartaric acid/tartrate Feigl tests (Table 1). Good matches for the HPLC chromatogram and UV-visible spectrum at a retention time of 1.58 min (Fig. 35) were obtained from a "King Midas" mixed fermented beverage sample, Near Eastern resinated wine samples, and modern barley.

Based on the chemical evidence, it then appears likely that the "beer mug" from the Citadel at Mycenae was filled with a mixed fermented beverage. It seems likely that the famous Golden Cup of Nestor (Karo 1930–31: pl. 210) from the same site contained the same libation (see further, below).

Editors' note: The MASCA result that the "beer mug," EUM 195, tested positively for barley – and thus could have once contained a mixture of wine, honey/mead, and barley beer – was not included in the Catalogue. This is additional information to that previously published.

7. Late Minoan IIIC1 Chamalevri (ca. 1190–1130 B.C.)

EUM 180 Baking basin, wall/base sherd T&M 149

The sample from a so-called "baking basin" (EUM 180) was too small for a DRIFTS analysis, but it gave a positive Feigl test for tartaric acid and the HPLC results (Fig. 36) gave good matches with an early New Kingdom plaster grape-treading installation at Tell el-Dab`a in the Nile Delta (Bietak 1985; McGovern 2000a: 74–77) and Near Eastern resinated wine samples. Perhaps, the unusually shaped vessel, with holes on either side and a spout, was used to prepared a special grape or wine sauce – not for coq-au-vin (since the domesticated chicken is of East Asian origin), but maybe a comparable game bird.

EUM 188 Tripod cooking pot, wall/base sherd T&M 161

The IR spectrum (Fig. 37) for a tripod cooking pot (EUM 188) from the site had the characteristic absorptions of tartaric acid/tartrate (Table 2), which was also borne out by a Feigl spot test, and a tree resin. Even though there was some indication of oxalate in the IR spectrum, the spot test was negative for this compound. The HPLC results at retention times of 1.57 and 1.62 min yielded matches for "King Midas" tomb beverage and food samples, the plaster grape-treading installation at Tell el-Dab`a, Near Eastern resinated wine samples, the Chamalevri baking tray, and two Chania vessels containing the mixed beverage. Presumably, grape, barley, and honey, whether fermented as a beverage or not, were standard ingredients in the cuisine at this time, as well as through the classical period and up to the present (see Dalby 1996), and were especially used to make savory stews.

8. Commentary

a. Resinated Wine

To date, the analyses of the Myrtos Phournou Koryphe pithoi, dating to ca. 2200 B.C., represents the earliest chemical evidence for resinated wine from ancient Greece (see p. 180). Resinated wine,[2] however, has a much earlier pedigree, dating back as early as 5400 B.C. in the northwestern Zagros Mountains of Iran (McGovern, *et al.* 1996 and 1997) and possibly as early as 6000 B.C. in Transcaucasia and eastern Anatolia (MASCA laboratory, unpublished analyses). In fact, as analyses by my laboratory have made clear, resinated wine was the rule rather than the exception in the ancient world, from Neolithic times down to the Byzantine period. The terpenoids in tree resins serve to protect the alcohol in the wine from being converted by bacteria to acetic acid (vinegar), and every competent winemaker wants to avoid that! The preservative and medicinal effects of tree resins must have been appreciated at an early date, and their use in wine continued to expand in later times, until it dominated the pharmacopeias of literate civilizations of the ancient world, particularly Greece.

Terebinth tree resin would appear to have been the resin of choice in the ancient world. Its characteristic triterpenoids were detected in an Apodoulou conical small bowl (above),

[2] Editors' note: not retsina, wine with pine resin, as defined in the Project.

and the analyses of many other ancient Near Eastern and Mediterranean wine samples from different regions and periods are consistent with its use as an additive in those, as well. According to the 1st century A.D. Roman encyclopedist, Pliny the Elder (*Historia naturalis*, bk. 14), it was the "Queen of Resins." However, the most famous and expensive tree resin additive to Roman wine was myrrh, which came from the Arabian peninsula and the Horn of Africa. This resin even has an analgesic effects, so that if the desired goal of preventing the wine from going to vinegar or covering up off-odors or tastes failed, at least one's senses were numbed.

It should be noted that many of the amphoras on board the late 14th century B.C. merchantman that went down off the coast of southern Turkey at Ulu Burun were as much as a third full of terebinth resin nodules and chunks. Beck, *et al.*'s (see p. 19) analyses of the ancient resin from this shipwreck provided a chemical match for the resin in the Apodoulou wine. Analyses of the same samples by the MASCA laboratory support this conclusion. The resin from the Ulu Burun jars has also tested positive for tartaric acid/tartrate, so it seems likely that the amphoras were originally filled with wine or that the terebinth resin had been used in processing grapes or wine (see McGovern 1997). As a space-saving measure, it makes sense to ship jars of wine containing extra resin. Only a finite amount of resin would dissolve in the wine. Once the wine were decanted off, the extra resin could have been used for incense, medicine, or as a preservative (including embalming).

As our Near Eastern investigation of early wine made clear, if winemaking is best understood as an intentional human activity rather than a seasonal happenstance, then the Neolithic period, from about 8500 to 4000 B.C., is the first time in prehistory when the necessary preconditions for this momentous innovation came together. Once humans were settled into permanent villages in the Neolithic, based on the first domesticated plants and animals, the conditions were ripe not only for experiencing and elaborating upon wine's psychotropic effects, but also for developing more predictable means of assuring a better quality wine and a more productive grapevine. Pottery, which was invented at this time, was ideal for forming shapes such as narrow-mouthed vats and storage jars, for producing and keeping wine. Wine was evidently part of everyday "Neolithic cuisine," which includes many other foods and beverages – including bread, beer, and many meat and cereal entrées – that we enjoy today.

Is it possible that wine was already being made in Greece in Neolithic times? Unfortunately, the *Archaeology Meets Science* Project did not resolve this issue. Pottery from one Neolithic site – the Cave of Gerani – was investigated by Curt Beck's laboratory (see Beck, *et al.*, pp. 32–33; Craig, pp. 121–124). While there was evidence of animal and vegetable fats, as well as olive oil, possibly components of stews, no evidence of what was drunk has yet been found. Seeds of the wild Eurasian grape (*Vitis vinifera sylvestris*) have been recovered from the Franchthi Cave in the Argolid of the Peloponnese, dating to the late Palaeolithic/Mesolithic periods (ca. 11000 B.C.), and many later Neolithic sites throughout Greece have yielded comparable evidence. Yet, unquestionably domesticated grape pips (*Vitis vinifera vinifera*) do not make their appearance in Greece until the Early Bronze Age (Renfrew 1995), at the same time that Myrtos Phournou Koryphe is flourishing.

Given the modern distribution of the wild Eurasian grape (see McGovern, *et al.* 1997: 18), which includes Greece and Crete, one might argue that viticulture and resinated wine arrived via Turkey or Balkans. This scenario would fit the archaeological evidence for a "wine culture" establishing itself first in the Near East and then radiating out from there in time and space. Prestige exchange of wine and special wine-drinking ceremonies among elite individuals, as can be documented for Mycenaean palace life (Wright 1995) and as best exemplified by the Classical Greek *symposion*, encouraged the adoption of winemaking and the successive transplantation or cloning of the domesticated grapevine in areas where even the wild grape had never grown. Other considerations, however, go against a transference of viniculture from the north or east into Greece, and fit better with its introduction from Egypt into Crete.

Egypt had begun transplanting the domesticated Eurasian grapevine and developed a thriving winemaking industry in the Nile Delta by at least 3000 B.C. (Dynasty 1) (see McGovern *et al.* 1997 and McGovern 1998). The Egyptian hieroglyph for grapevine, vineyard or wine (*irp*), which is attested about the same time, is clearly the forerunner of the Linear A and B signs of Late Minoan and Mycenaean times (Palmer 1995; also see Palmer 1994). The vocabulary of a technology such as winemaking – the actual script in this instance – very often follows along with its transference from one culture to another. All the signs show the evident care that was taken in trellising and caring for the vine, indicating that viticulture and winemaking were already well advanced in Egypt by around 3000 B.C., probably having been introduced by Levantine specialist vintners into the Delta.

Nevertheless, the Linear A and B text are some 700 years later than the earliest evidence of resinated wine from Myrtos Phournou Koryphe. If the domesticated grapevine, along with winemaking, had already been transplanted to Crete from Egypt by at least ca. 2200 B.C., then archaeological evidence is needed to sustain the hypothesis. Trade between Egypt and Crete is well attested for the Middle and Late Bronze Age. In addition, the Early Minoan site of Myrtos Phournou Koryphe, on the southern shore of Crete, is located on a natural landfall and at the terminus of a well-traveled maritime route for ships crossing the Mediterranean from Egypt.

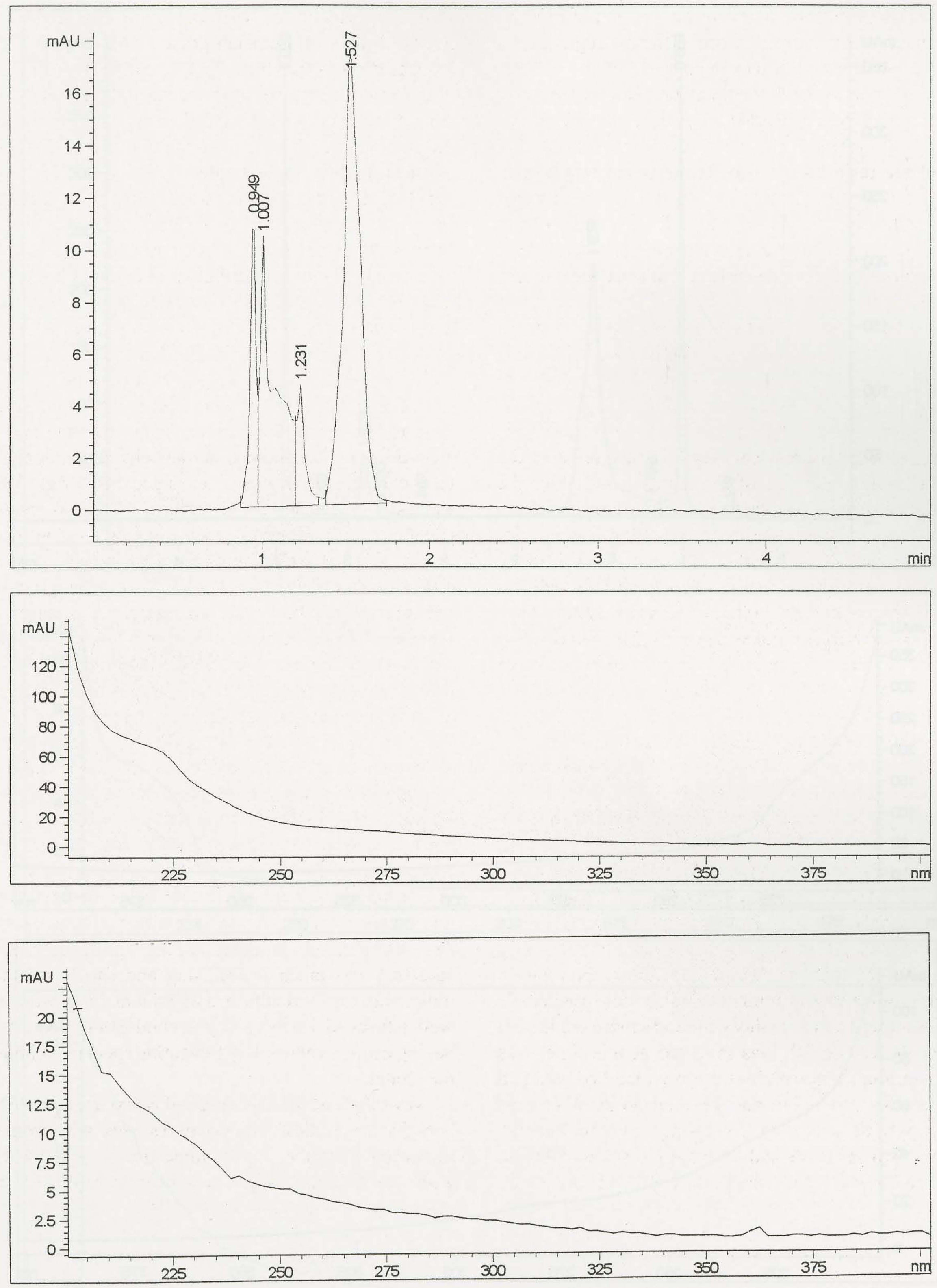

Figure 20 *Chania Splanzia (EUM 36): liquid chromatogram and UV absorption spectrum at 1.55 and 1.62 min*

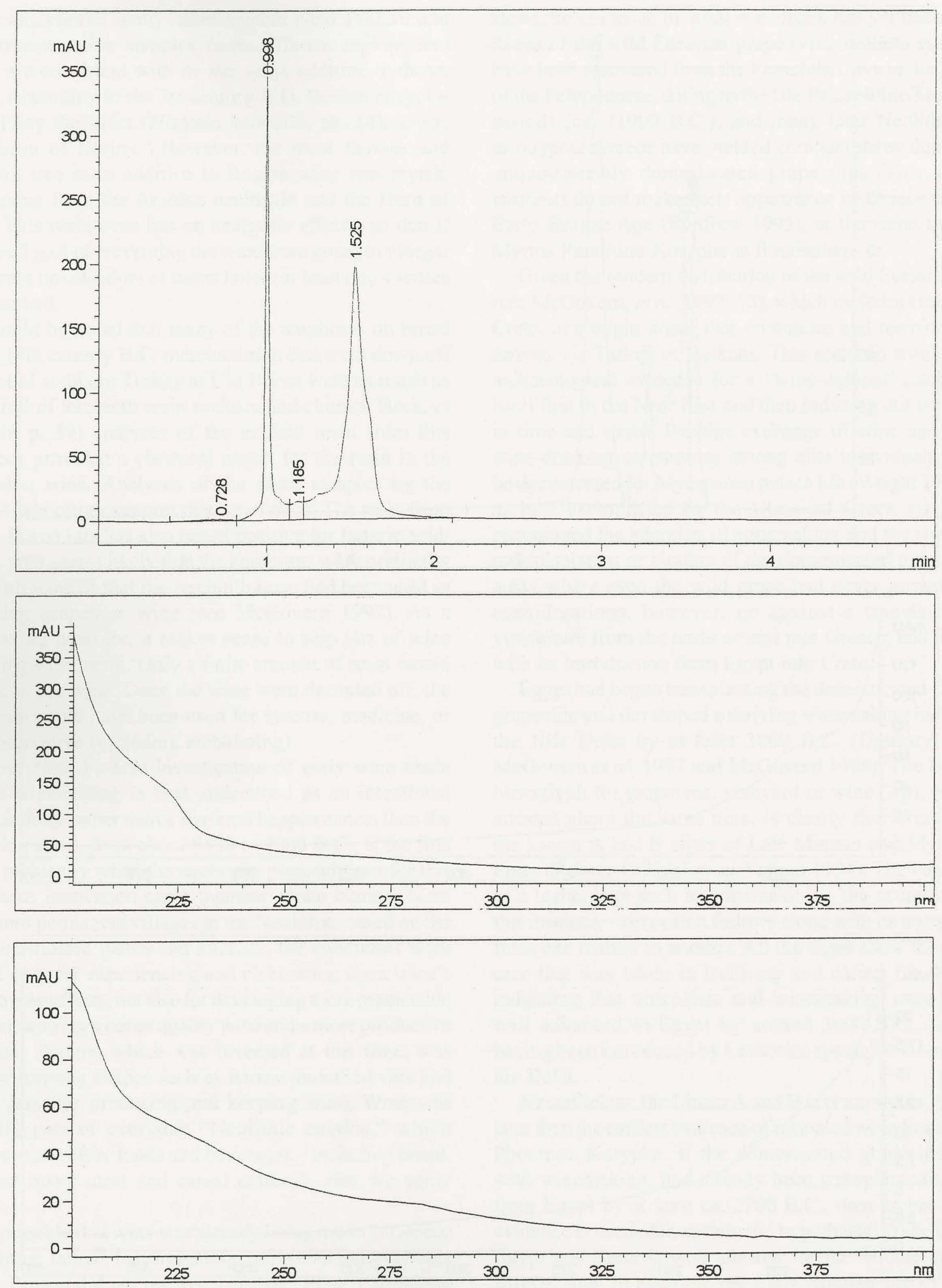

Figure 21 *Chania Splanzia (EUM 47): liquid chromatogram and UV absorption spectrum at 1.52 and 1.62 min*

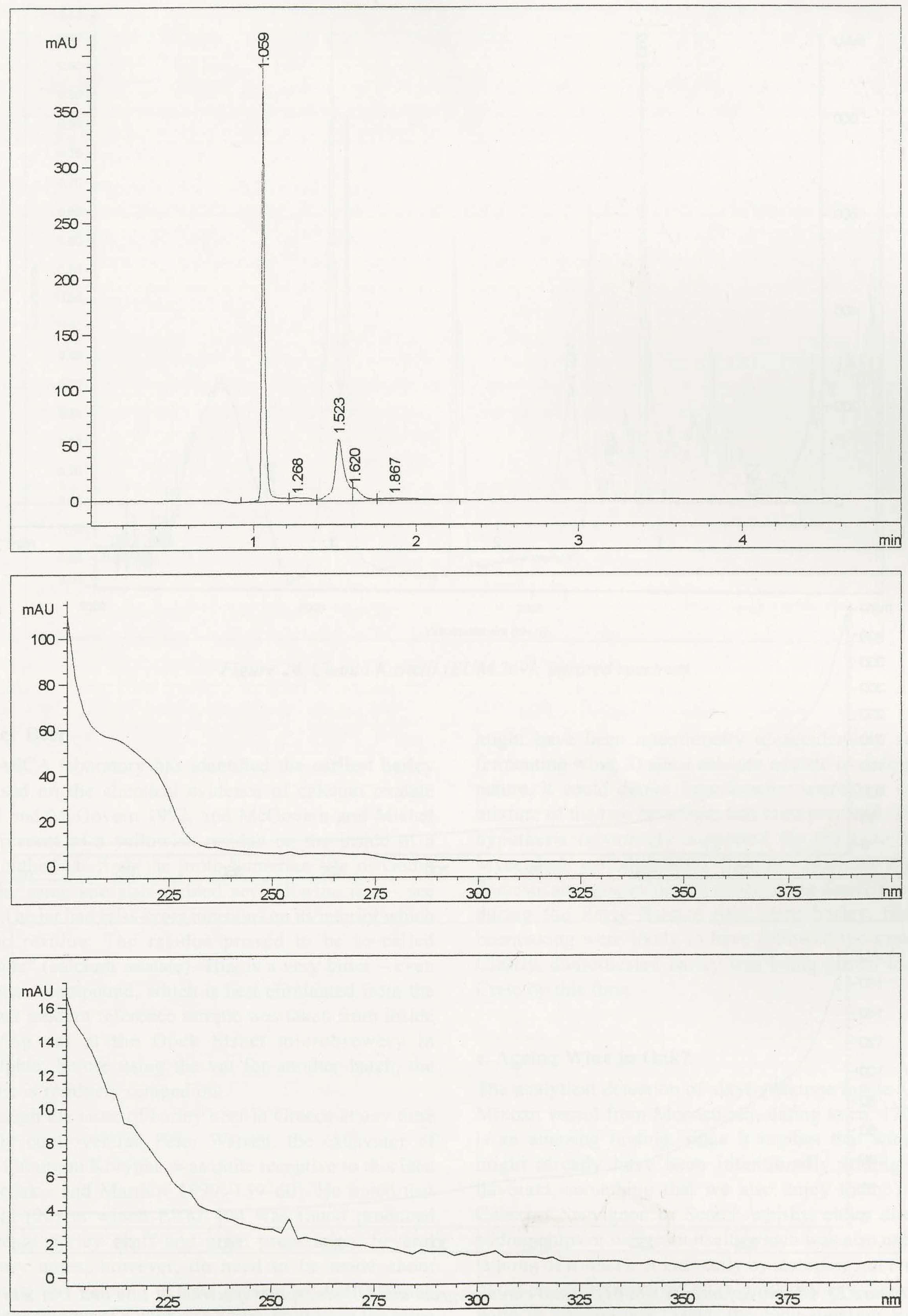

Figure 22 *Chania Splanzia (EUM 58): liquid chromatogram and UV absorption spectrum at 1.52 and 1.62 min*

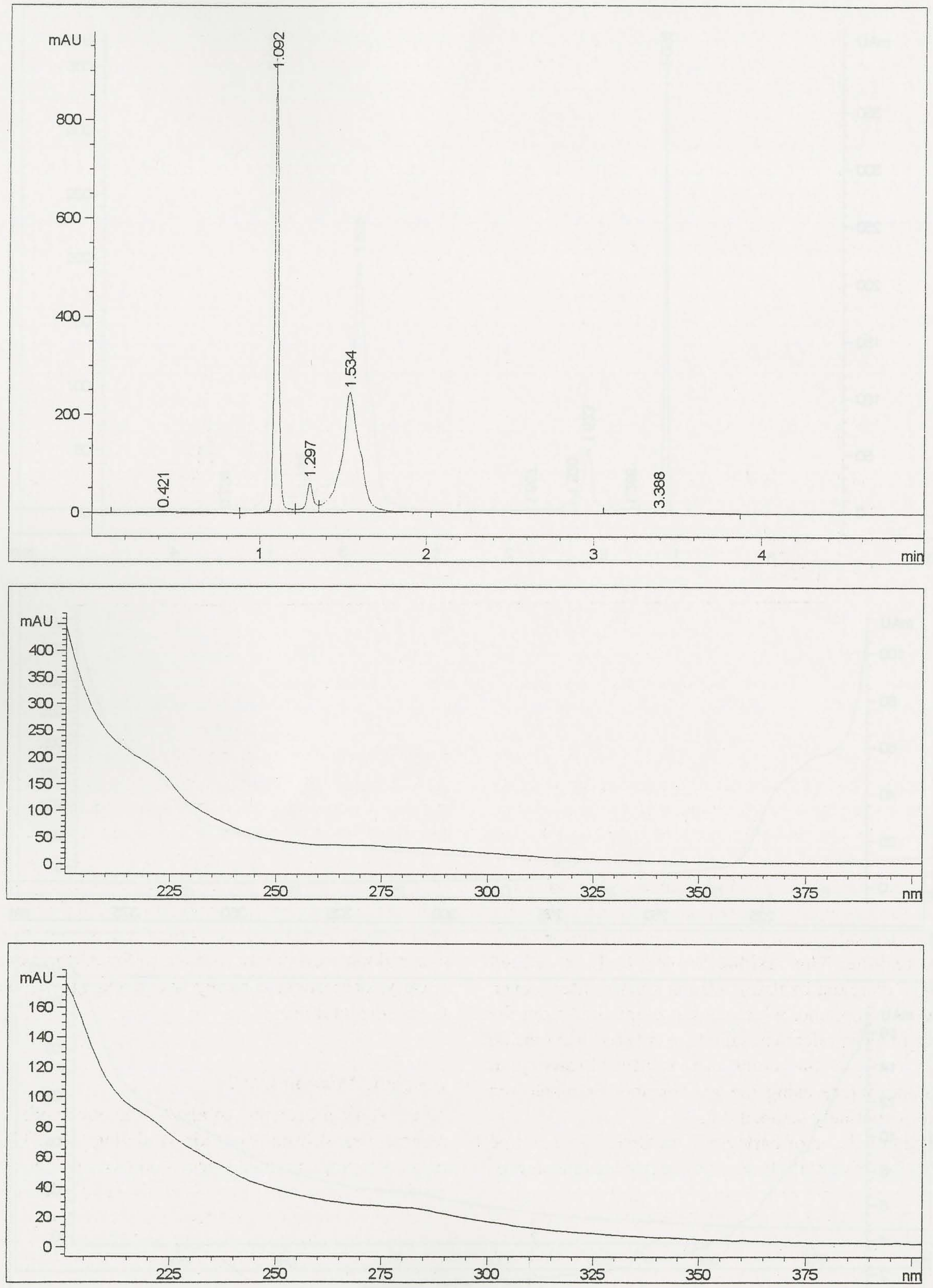

Figure 23 *Chania Splanzia (EUM 61): liquid chromatogram and UV absorption spectrum at 1.53 and 1.61 min*

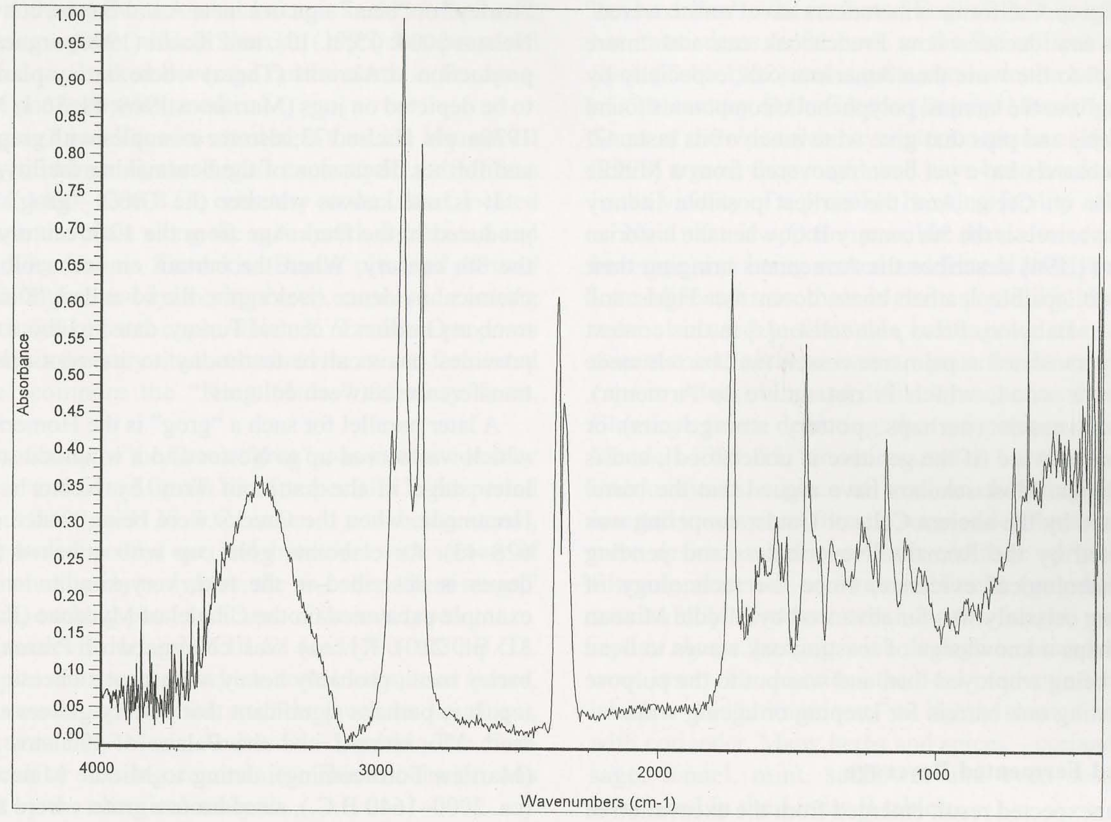

Figure 24 *Chania Kastelli (EUM 269): infrared spectrum*

b. Barley Beer

The MASCA laboratory has identified the earliest barley beer based on the chemical evidence of calcium oxalate (Michel and McGovern 1992, and McGovern and Michel 1993), present as a yellowish residue on the inside of a wide-mouthed jar from the proto-Sumerian site of Godin Tepe (the same site also yielded several wine jars – see above). The jar had criss-cross incisions on its interior which held the residue. The residue proved to be so-called "beerstone" (calcium oxalate). This is a very bitter – even poisonous – compound, which is best eliminated from the brew. Our modern reference sample was taken from inside a brewing vat at the Dock Street microbrewery in Philadelphia; before using the vat for another batch, the beerstone is routinely scraped out.

Although the issue of barley beer in Greece at any time is highly controversial, Peter Warren, the excavator of Myrtos Phournou Koryphe, was quite receptive to this idea (see Tzedakis and Martlew 1999: 159–60). He noted that the room (20) in which EUM 104 was found produced evidence of barley chaff and grain preparation. Several cautionary notes, however, do need to be made about interpreting any calcium oxalate present as due to barley beer: 1) the finding of a wine and barley product in the same jar may be due to reuse of the same vessel, 2) barley grains might have been intentionally or accidentally added to fermenting wine, 3) since calcium oxalate is widespread in nature, it could derive from another source, or 4) a true mixture of the two beverages had been prepared. The latter hypothesis is strongly supported for the Late Minoan-Mycenaean period (below). It is also plausible that if the domesticated grapevine and winemaking derive from Egypt during the Early Bronze Age, then barley, bread and beermaking were likely to have followed the same route. Clearly, domesticated barley was being grown locally on Crete by this time.

c. Ageing Wine in Oak?

The analytical detection of alkyl-γ-lactone inside a Middle Minoan vessel from Monastiraki, dating to ca. 1700 B.C., is an amazing finding, since it implies that winemakers might already have been intentionally adding an oak flavorant, something that we also enjoy today in a fine Cabernet Sauvignon or Scotch whisky, either directly by adding chips or oak resin itself (which was also used in the tanning of leather), or indirectly by stomping out the grapes in oaken winepresses or, more provocatively, "ageing" the wine in oak barrels. Thus, the long-standing European tradition of ageing wine in oak barrels might have a much earlier pedigree. California winemakers have "rediscovered" in the last few decades how French oak can add "more complexity" to the wine than American oak, especially by "mellowing" out the tannins, polyphenolic compounds found in grape skins and pips that give wine much of its taste. Of course, no barrels have yet been recovered from a Middle Minoan site on Crete. And the earliest possible literary reference to barrels is the 5th century B.C. when the historian Herodotus (1.194) describes the Armenians bringing their wines in collapsible leather boats down the Tigris and Euphrates to Babylon. *Bikos phoinikeiou[s]* in this context is variously translated as palm tree vessels (i.e., barrels made of palm tree wood, which is not native to Armenia), Phoenician vessels (perhaps, pottery storage jars) or Phoenician/red wine (if the genitive is understood), and is highly dubious. Most scholars have argued that the barrel was invented by the ancient Celts or Gauls; coopering was then adopted by the Romans. Nevertheless and pending more archaeological evidence, since the technology of shipbuilding certainly was far advanced by Middle Minoan times, perhaps a knowledge of toasting oak staves to bend them was being employed then and was put to the purpose of constructing oak barrels for keeping or ageing wine.

d. A Mixed Fermented Beverage

A totally unexpected result emerged from the excavation of a Late Minoan IA (ca. 1600–1480 B.C.) "cult area" with many "altars" surrounded by the burnt remains of sheep, goat and cattle, carried out by Maria Andreadaki-Vlazaki along Splanzia and Daskaloyiannis Streets in Chania (Minoan Kydonia). Our chemical analyses showed that a different kind of beverage was being drunk and/or ceremonially presented in conical cups and other pottery types in Late Minoan IA than in the Middle Minoan II period. The libation combined resinated wine, barley beer and honey mead, what might be described as a kind of Greek "grog" or "toddy," as amusingly portrayed and placed within its larger cultural context by Stephanie Pain (1999).

This is not the place to describe the types of conical cups and the evidence for their astonishing numbers and significance, particularly in cult contexts. The conical cup has been called a "nightmare vessel," which can have many purposes (Wiener 1984 and 1990). However, based on the chemical analyses presented above, we would propose that the main function of the various types of conical cups was for ceremonial drinking and libations.

We know that wine was an important commodity in palace life, since the wine ideogram appears often in Linear A and B texts at Mycenae, Pylos, Knossos, Phaistos, Chania, Kato Zakros, and elsewhere (Palmer 1985). Moreover, a "honeyed wine" is referred to in one of the Pylos texts. But the objection may be raised that if barley beer were an important commodity, why is it nowhere to be found in the tablets? Although debatable, some scholars argue for a "barley" or "beer" sign in Linear A and B (see, conveniently, Nelson 2004: 15, n. 13), and Koehl (1990) argues for beer production at Akrotiri (Thera) where barley plants appear to be depicted on jugs (Marinatos 1969; Pl. 36.1; Marinatos 1970a: pls. H.c and 73; also see examples with grape clusters and further discussion of the beermaking facility, below).

It is not known whether the Greek "grog" was still produced in the Dark Age from the 12th century down to the 8th century. When the curtain on archaeological and chemical evidence rises again, the so-called "King Midas" tomb at Gordion in central Turkey, dated to about 730 B.C., provides provocative testimony to its continuation and transference between cultures.

A later parallel for such a "grog" is the Homeric *kykeon*, which was served up to Nestor and a wounded soldier at a later stage in the battle of Troy by Nestor's mistress, Hecamede, when the Greeks were being routed (*Iliad* 11: 628–43). An elaborate gold cup with attached figures of doves is described in the text, very similar to an actual example excavated on the Citadel of Mycenae (Karo 1930-31: pl. 210). *Kykeon* was comprised of Pramnian wine, barley meal, probably honey, with goat's cheese grated on top. It is perhaps significant that pottery graters are known from Monastiraki and the Palace of Phaistos on Crete (Martlew Forthcoming), dating to Middle Minoan IB–IIA (ca. 2000–1640 B.C.), since bronze graters were a standard burial good in Iron Age warrior tombs in Greece and Italy (Ridgway 1997). However, the only grater submitted for organic residue analysis as part of *Archaeology Meets Science* project, EUM 242, yielded evidence of olive oil/plant oil (Beck, *et al.*, this volume), *Kykeon* is probably best translated as "mixture," and a range of ancient Greek texts (see Delatte 1995, Richardson 1974, and Ridgway 1977), extending down to Plato and the Eleusinian Mysteries, suggest that a large variety of ingredients (herbs, spice, wine, milk, honey, oil, and water) might be included in the brew.

The pharmacological properties of this brew – whether analgesic or psychoactive is unclear, but certainly exceeding what can be attributed to a high alcohol content – is implied in the Nestor account, as well as elsewhere in Homer (e.g., when Circe changed Odysseus's companions into pigs with *kykeon* and a *pharmaka* in *Odyssey* 10: 229–43). One can debate whether Pramnian wine, which goes into *kykeon*, is an herbal wine or a kind of *grappa*, whether the barley is raw, roasted or fermented, and so forth. The main point is that the mixed fermented beverage or "Minoan ritual cocktail", which has now been identified chemically, probably bears some relationship to the *kykeon* of Greek heroic times. As yet, however, no spice or herb has been chemically identified in the Greek "grog," although references to such in the Linear A and B texts and the probable presence of rue, a narcotic and stimulant, in a cooking pot from Mycenae (Beck *et al.*, see p. 42) are highly suggestive

(below). Other narcotic substances – such as henbane, mandrake or opium, which Sherratt (1995) has proposed were added to a mixed beverage farther north in Europe – have also not been confirmed.

The "grog" was likewise attested at the Late Minoan III Cemetery of Armenoi, the largest excavated Late Minoan IIIA/B (ca. 1400–1200 B.C.) cemetery on the island, located inland from the coast along the main north-south road and excavated by Yannis Tzedakis. Burial pits and *dromoi* contained fragmented *kylikes* (goblets), cups, and cooking pots. Both *kylikes* and cups, which Y. Tzedakis proposes were used in a funerary ritual contained the mixed fermented beverage (compare the "King Midas" funerary feast, below).

The popularity of the Greek "grog" was most evident by Mycenaean and Late Minoan times, especially in the period from about 1400 to 1130 B.C., when it was being stored, prepared, served, poured out, and drunk in a wide variety of vessels, including *rhyta, kylikes*, the so-called "beer mugs," stirrup jars, cooking pots, and cups of various types.

At Chamalevri during LM III C1 (ca. 1190–1130 B.C.), well-cut pits and trenches, which contained animal bones, cooking vessels and special artifacts (such as figurines), were excavated by Maria Andreadaki-Vlazaki. The finds point to cult or feasting ceremonies. This conclusion was borne out by the chemical analyses.

e. Kylikes

The *kylikes* are of special interest, because they are depicted being "held high" on fresco scenes at Knossos and Pylos (see Wright 1995: fig. 18.8, conveniently, for one example from Knossos) that have clear ceremonial or religious significance. The goblets, which include handleless types of coarser, undecorated ware as well as more elegant decorated types, were probably also used to drink or libate the mixed beverage.

f. Rhyton

Another vessel type of possible significance in understanding the "Greek grog" is the *rhyton*. Although our laboratory did not analyze any *rhyta*, John Evans (this volume) reports that a rhyton found at Midea (Late Helladic III A2, ca. 1370–1190 B.C.) on the Mainland, yielded evidence of wine and barley beer. This vessel type, which always has a hole at its bottom, was presumably used to pour a liquid through it like a funnel.

Robert Koehl (1981 and 1990) has discussed the various *rhyton* types in his publications, where he presents cogent evidence for transferring and filtering liquids by such vessels. When they are globular or ovoid and narrower mouthed than the conical type, they can even be used like chemical pipettes, to draw up and hold liquids in place by simply placing a hand or thumb over the upper opening. Parallels can be drawn to the medieval English "toddy-lifter," which has antecedents as far back as the 3rd millennium B.C. in Syria (Tubb 1982) and is quite similar to the later *klepsydra* of 6th century B.C. Greece (Dayagi-Mendels 1999: 69). Some of the *rhyta* also have interior strainers, and as Koehl (1990) argues, they might well have been used to filter beer in the vicinity of a probable brewing facility at Akrotiri.

Now that it appears possible that a mixed fermented beverage was being served and libated in Mycenaean and Late Minoan times, there is also a possibility that the *rhyta* were also used to filter this beverage or one of its components, and perhaps even to pour the beverage out into cups in a flourishing and difficult manner as shown on later Classical vases depicting the symposium (see Dayagi-Mendels 1999: 85, for one example). For the *rhyta* without interior sieves, a piece of wool or cloth might have been inserted to serve as a filter. If some added flavor or stimulant were desired, a spice or herb could be sprinkled on the filtering material or strainer. Koehl (unpublished) has successfully demonstrated how this might work with a replica *rhyton*, passing wine through a coriander-sprinkled wool insert. He describes the final product after tasting it, which is the "ultimate test," as lightly scented and flavored with coriander. Many herbs and spices – coriander, cumin, sage, fennel, mint, safflower and even sesame – are mentioned in the Linear B tablets.

Beck, *et al.* (see p. 42) reports finding two ketones specific to the herb genus *Ruta* (rue) in a tripod cooking pot (EUM 72) in the Citadel House Area (room 34) at Mycenae, dated to early LH IIIC (ca. 1190–1130 B.C.). Domesticated *Ruta graveolens* is found in Greece, as well as wild rue (*Peganum harmala*), although it is not clear whether the same marker compounds occur in the latter. No unequivocal archaeobotanical evidence has yet been obtained from Greek sites.

Assuming that rue was present in tripod cooking pot, EUM 72, then possibly it was one of the spices that could have been added to the resinated wine, attested for amphora EUM 67 (also confirmed for EUM 68 by Beck, *et al.*, p. 36), or to a mixed fermented beverage using a *rhyton*. The name for this herb derives from the Greek word *reuo* ("to set free"), which is particularly appropriate for a narcotic, medicinal agent. Because of its bitterness, it served to offset any sweetness of the beverage. Much later, it was a substitute for hops in European beer, which didn't become popular until the 17th century A.D. In medieval times, European barley beer was generally spiced with a variety of spices. So-called gruit ale, combining wild rosemary, yarrow and bog myrtle, was most common (Buhner 1998).

One may propose that resinated wine production and trade to other islands in the Aegean was well underway by the Late Bronze Age, as implied by the marvelous jugs with clusters of deep red grapes from Thera (Marinatos 1970b: pl. 561 and 1974: pl. 79), which occur as early as Late

Cycladic I in the 16th century B.C. The fine wines of the Levant, Near East, and Egypt were also appreciated, and imported in amphoras, the successor to the Middle Bronze Age "Canaanite Jar" (McGovern and Harbottle 1997 and McGovern 2000a).

g. Final Observations and Questions

Fermented beverages are of particular importance in understanding human innovation and cultural/technological development (see McGovern 2003). Except the Eskimos and the native peoples of Tierra del Fuego, humans have shown a remarkable propensity to develop independently alcoholic beverages from any available sugar source.

As one recent example, an archaeological chemical study of fermented beverages from ancient China was begun in 2000, which has since elucidated the chemical compositions of rice and millet wines dating to the Shang/Western Zhou dynasty, ca. 1250–1000 B.C. (McGovern, *et al.* 2004). These beverages were made using a different fermentation system than we are accustomed to in the west. Rather than malting, a variety of molds or fungi (e.g., *Aspergillus oryzae* and *Rhizopus oryzae*) convert the complex carbohydrates in grains to simple sugars, which are then fermented to alcohol and carbon dioxide by yeast. Since more than 50% of the superb bronze vessels of the Shang Dynasty, the earliest archaeologically attested period in China with city-states and kings, were used in drinking ceremonies and festivities, the advance of civilization there appears to have developed in tandem with an appreciation for fine drink. Today, China is still what can be called a "wine culture"; wine and distilled spirits are served at special meals and celebrations, with a protocol for how the toasting is done.

The Molecular Archaeological study of the Bronze Age vessels shows that Greece enjoyed a similar kind of wine culture, as it continues to do today. As was mentioned above, the results of our research yielded some surprises from what might have been expected when the project began several years ago. The discovery of Phrygian "grog" was also a completely fortuitous, serendipitous tie-in to the Greek evidence.

That the ancient Greeks prepared and drank barley beer also came as a surprise. Intriguingly, later Greek writers and gourmands dismissed beer as a barbarian drink, and resinated wine came to be mixed only with water. Most scholars have thus assumed that beer was never drunk by the Greeks. Yet, barley grows well on thin soils, and was already cultivated as early as the Neolithic period in Greece. Breadmaking, which employs many of the same techniques as beermaking, was well-established in ancient Greece, and, given the close contacts between Greece and Egypt where barley beer reigned supreme, the Greeks could have produced beer if they wanted. The available evidence, at present, suggests that they did not drink barley beer by itself, but mixed it with other fermented beverages. One may propose that this custom was introduced by peoples migrating into Greece from the north ca. 1500 B.C. A mixed fermented beverage, incorporating the available sugar resources (honey, likely saccharified wheat or barley, and possibly fruit such as apple and berries) and with added herbs, is documented in northern Europe as early as 3000 B.C. (Sherratt 1987; see Pain 1999, and Koch 2000a, 2000b and 2003).

One might ask what was the origin of the mixed fermented beverage that was served at the funerary feast of King Midas or one of his royal ancestors around 730 B.C., and does it have any relationship to the earlier Greek "grog?" And if there is a connection, why is the Phrygian "grog" not resinated? Possibly, the Phrygians perpetuated the tradition that was gradually displaced by diluted resinated wine in Greece. Many scholars are of the opinion that the ancient Phrygians, whom Midas ruled, migrated originally from northern Greece or the Balkans (Thrace or Macedonia) to central Turkey sometime after 1200 B.C. Presumably, a resinated wine was being produced there – although we are yet to carry out analyses of material from those regions. Farther north in Europe, however, fruit juices other than grapes (which are difficult to grow in northern climes) – such as cranberries and apples – were used (see Pain 1999). Tree resins might have been an optional additive there in making mixed fermented beverages. The long-standing European tradition probably owed its development to the idea that the environment had to be culled for potential sources of sugar, and that the more natural products with sugar that one could combine together in the fermentation tank, the higher the alcoholic content of the end-product would be. One may therefore propose that both the Late Bronze Greeks and Phrygians are tied to separate movements of peoples, including Indo-Europeans, who maintained their traditions of preparing a mixed fermented beverage and drinking it on special occasions. In Greece, which has been shown by the scientific analyses carried out under the auspices of this Project, to have had a long tradition of making resinated wine, including a pine-resinated variety comparable to retsina.

Molecular Archaeology promises to open whole new perspectives on the exciting history of foods and beverages in ancient Greece, as well its economy and social and religious customs. As has been discussed above, resinated wine dates back to the late 3rd millennium B.C. in the Aegean, and it was possibly being aged in toasted oak barrels, or at least coming into contact with oak at some time during the production process, by the early 2nd millennium (EUM 30) (see Beck, pp. 33–36). By the middle of that millennium, however, a mixed fermented beverage of resinated wine, barley beer and honey mead, had become a popular beverage in Greece. Greeks of the 1st millennium B.C. returned to their roots, as it were, and were more likely to mix or dilute their resinated wine only with water. Thus, although the classical Greek wine-set of krater, jug, ladle, and *kylix*/cup/mug/bowl had its origins in Late Minoan Crete

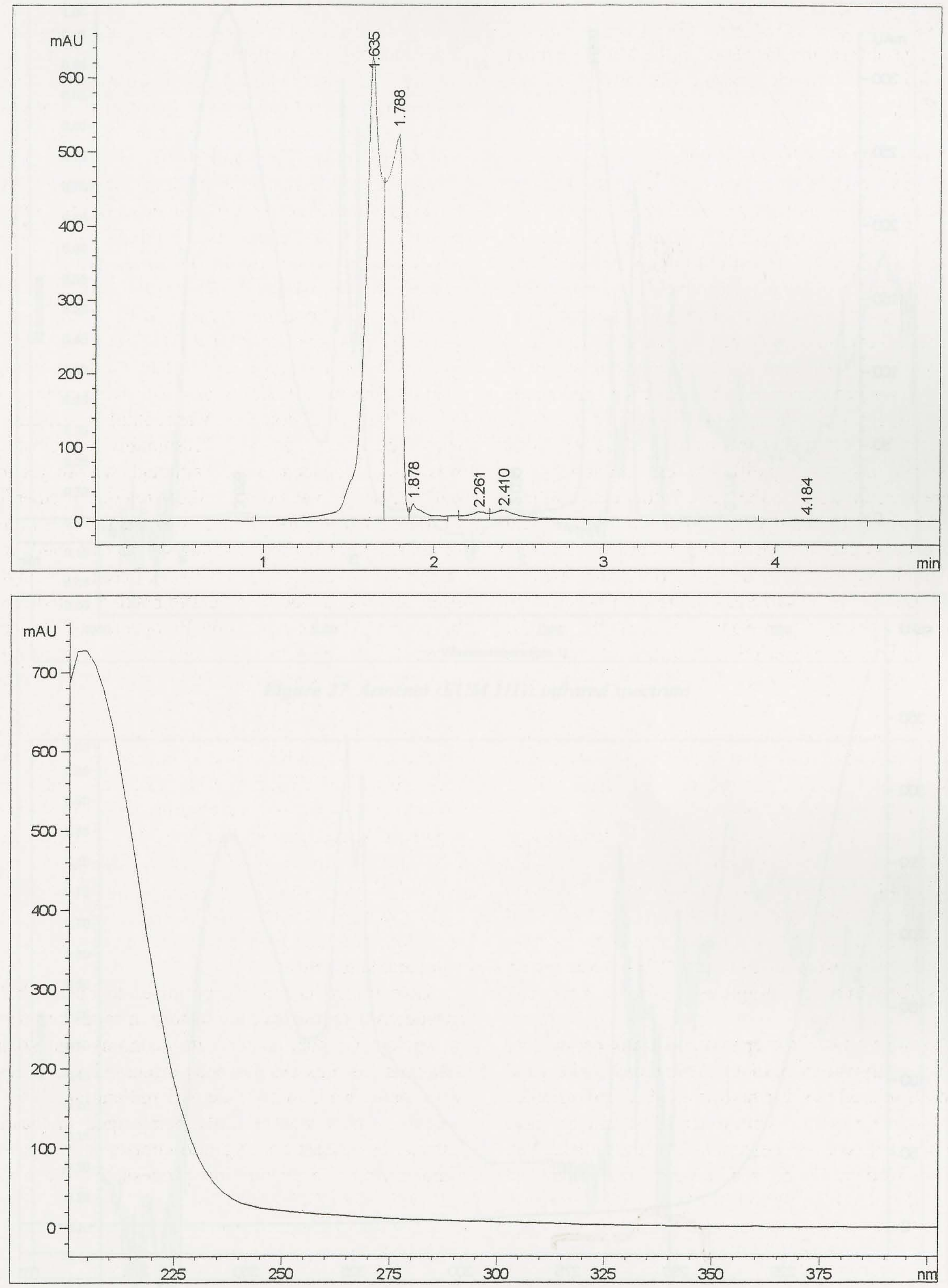

Figure 25 *Chania Kastelli (EUM 252): liquid chromatogram and UV absorption spectrum at 1.63 min*

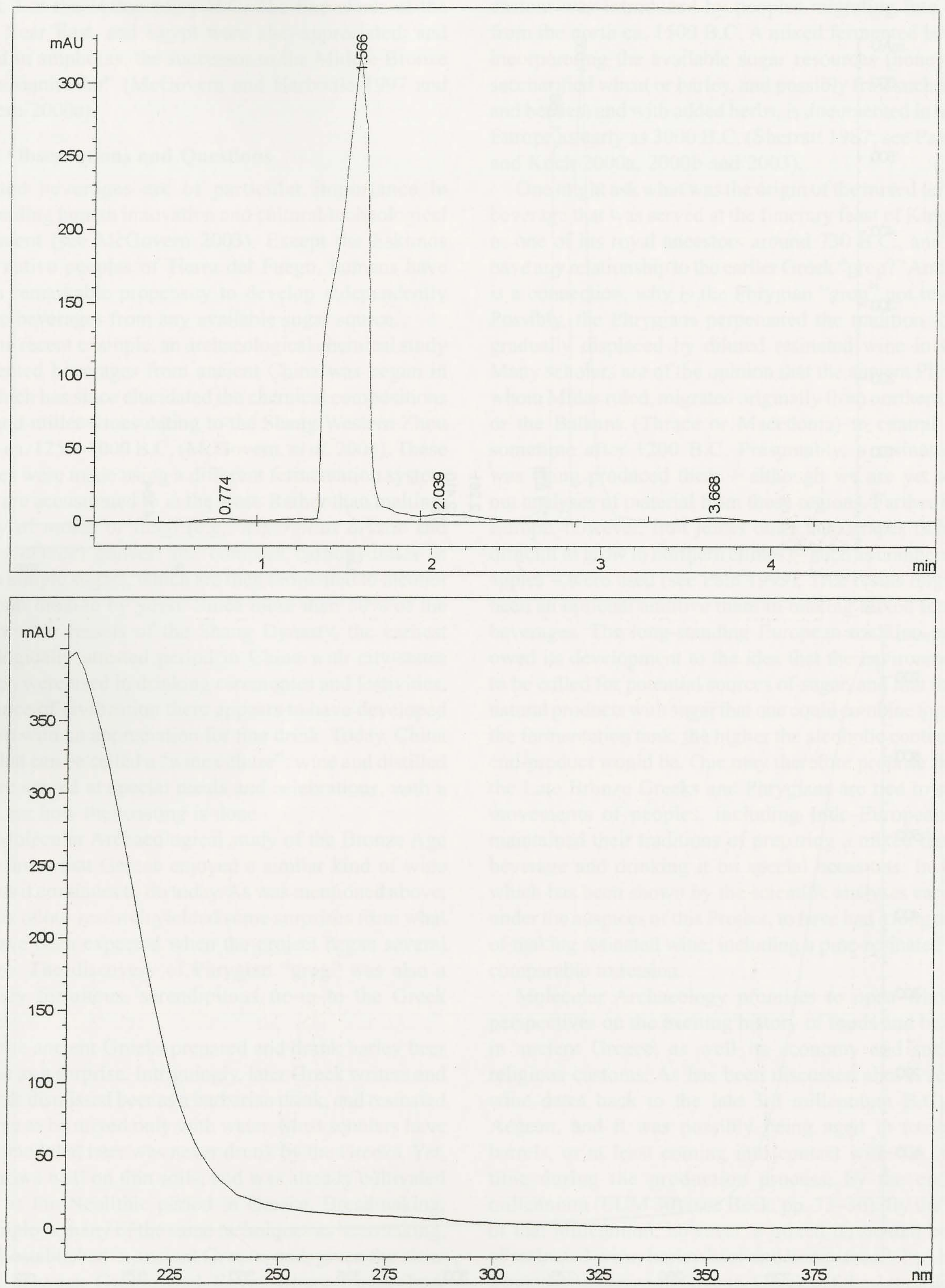

Figure 26 *Chania Kastelli (EUM 267): liquid chromatogram and UV absorption spectrum at 1.57 min*

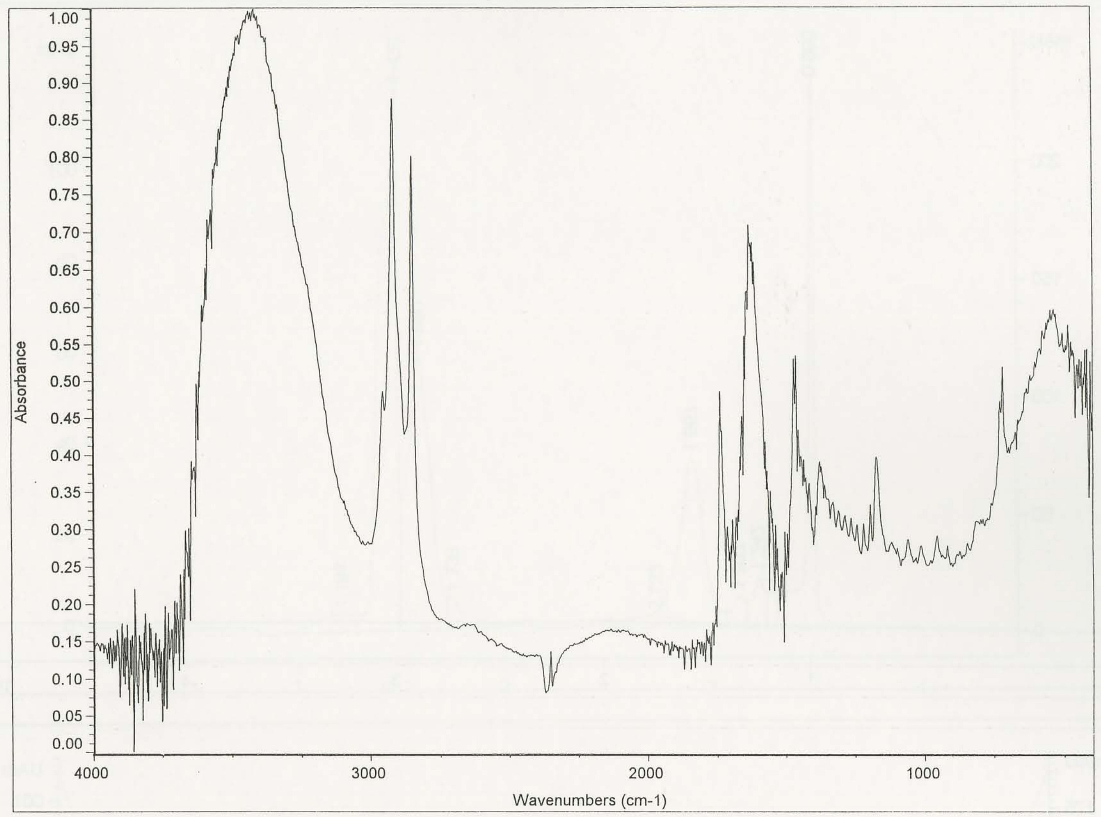

Figure 27 *Armenoi (EUM 111): infrared spectrum*

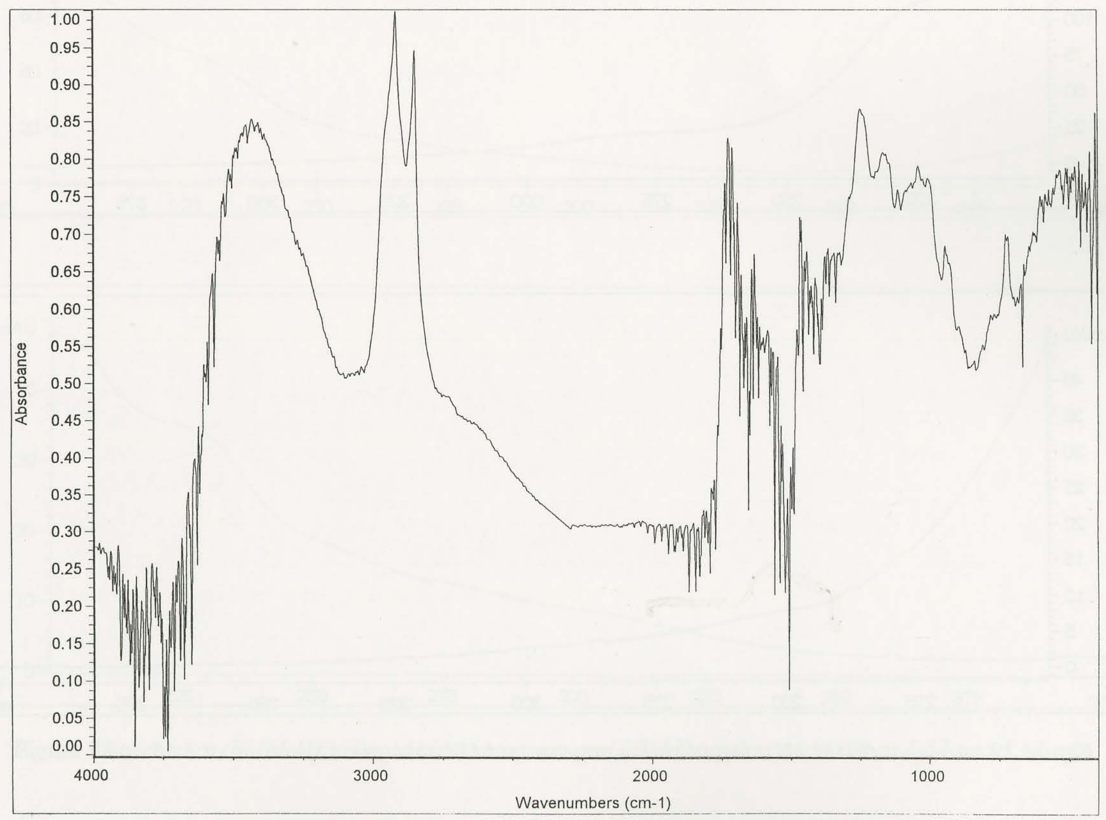

Figure 28 *Armenoi (EUM 122): infrared spectrum*

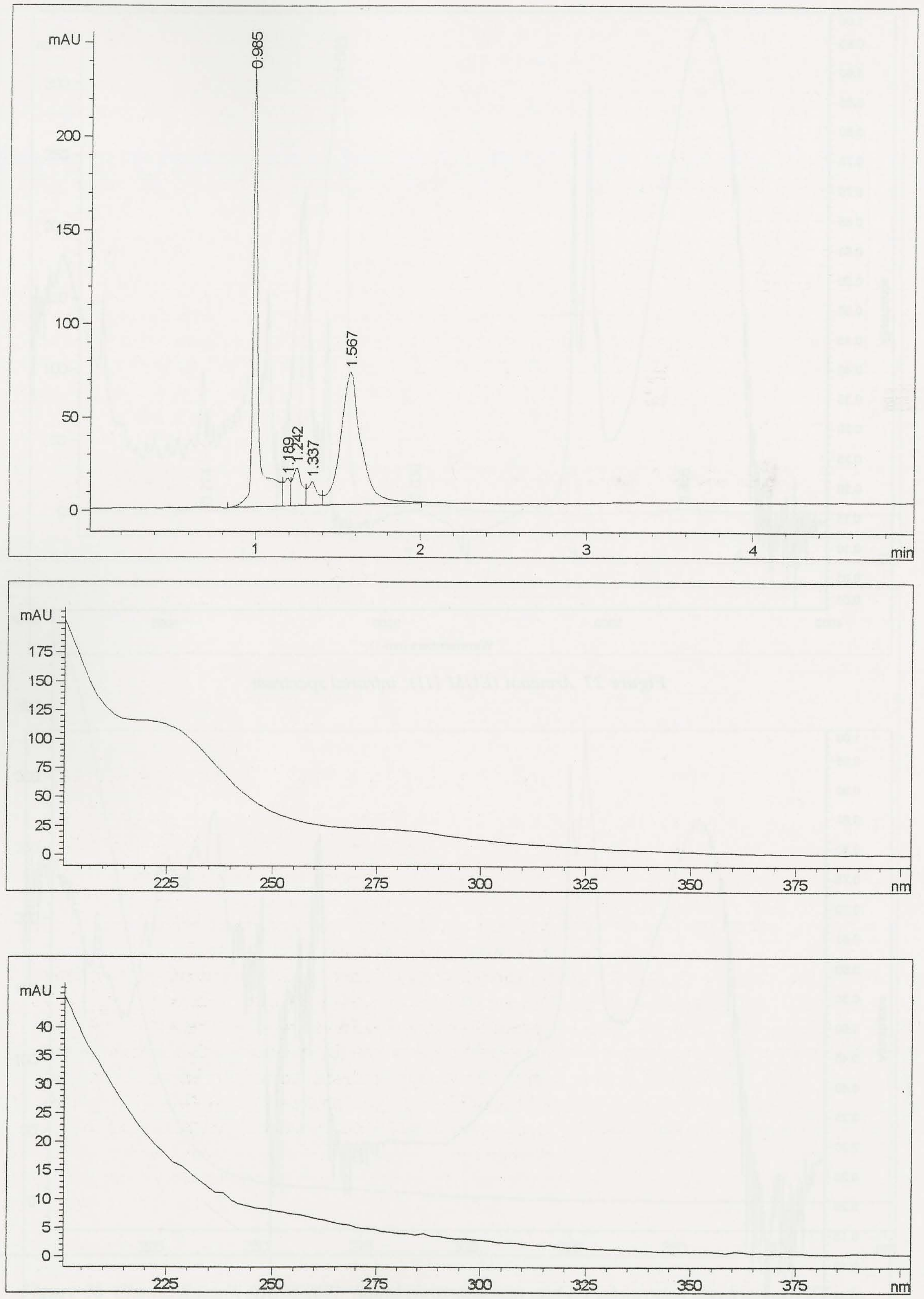

Figure 29 *Armenoi (EUM 111): liquid chromatogram and UV absorption spectrum at 1.55 and 1.64 min*

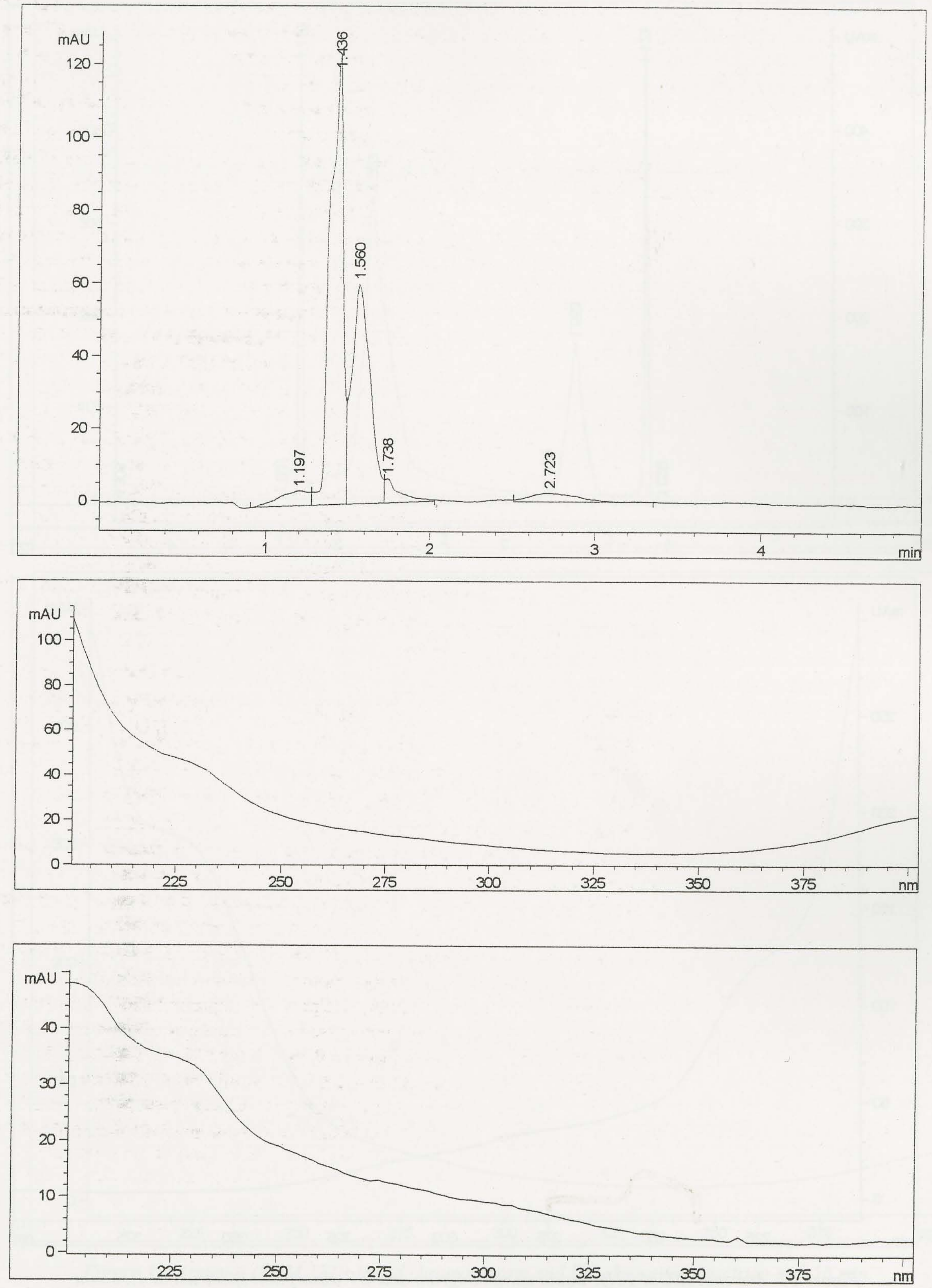

Figure 30 *Armenoi (EUM 116): liquid chromatogram and UV absorption spectrum at 1.57 and 1.61 min*

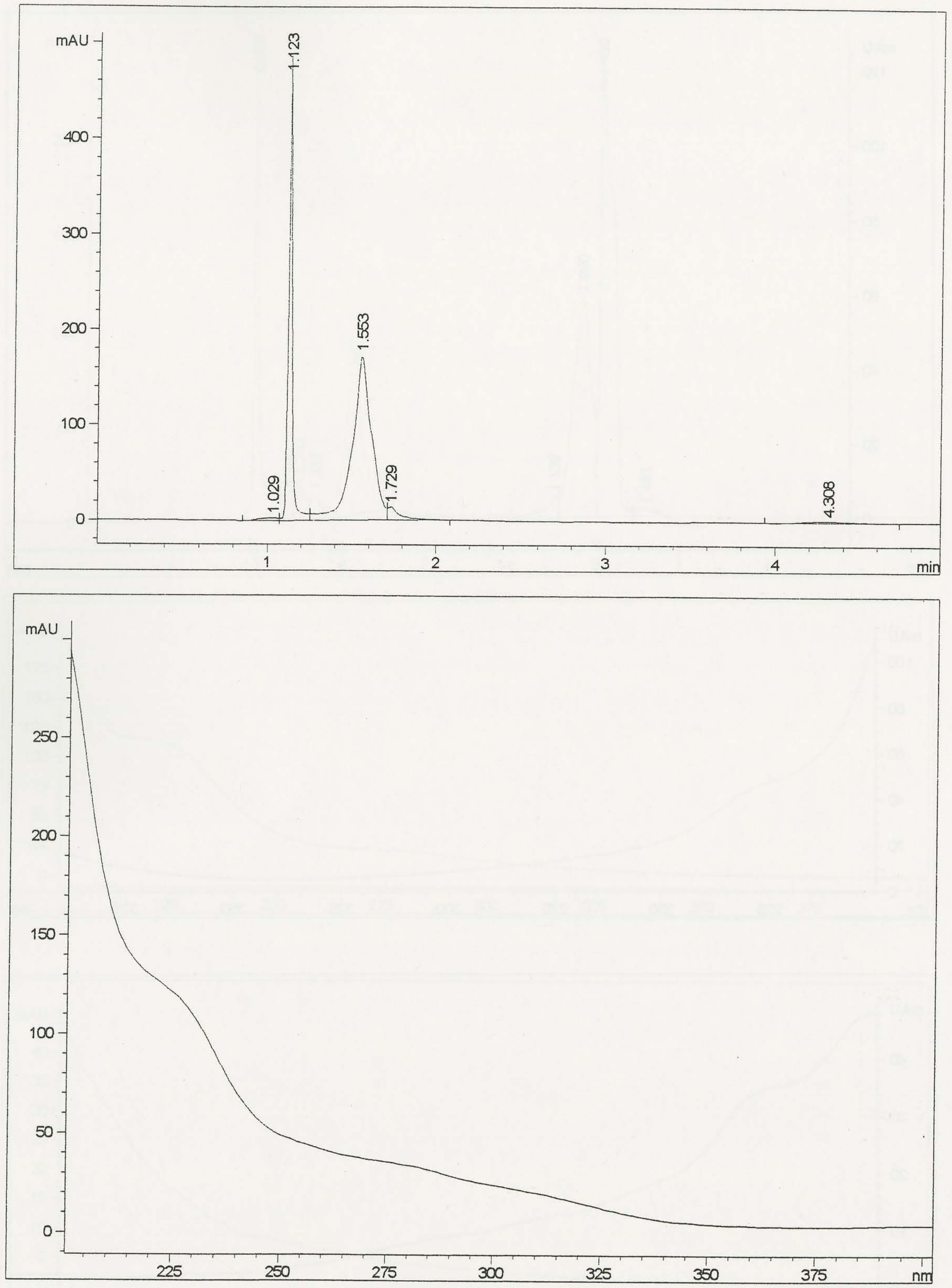

Figure 31 *Armenoi (EUM 121): liquid chromatogram and UV absorption spectrum at 1.56 min*

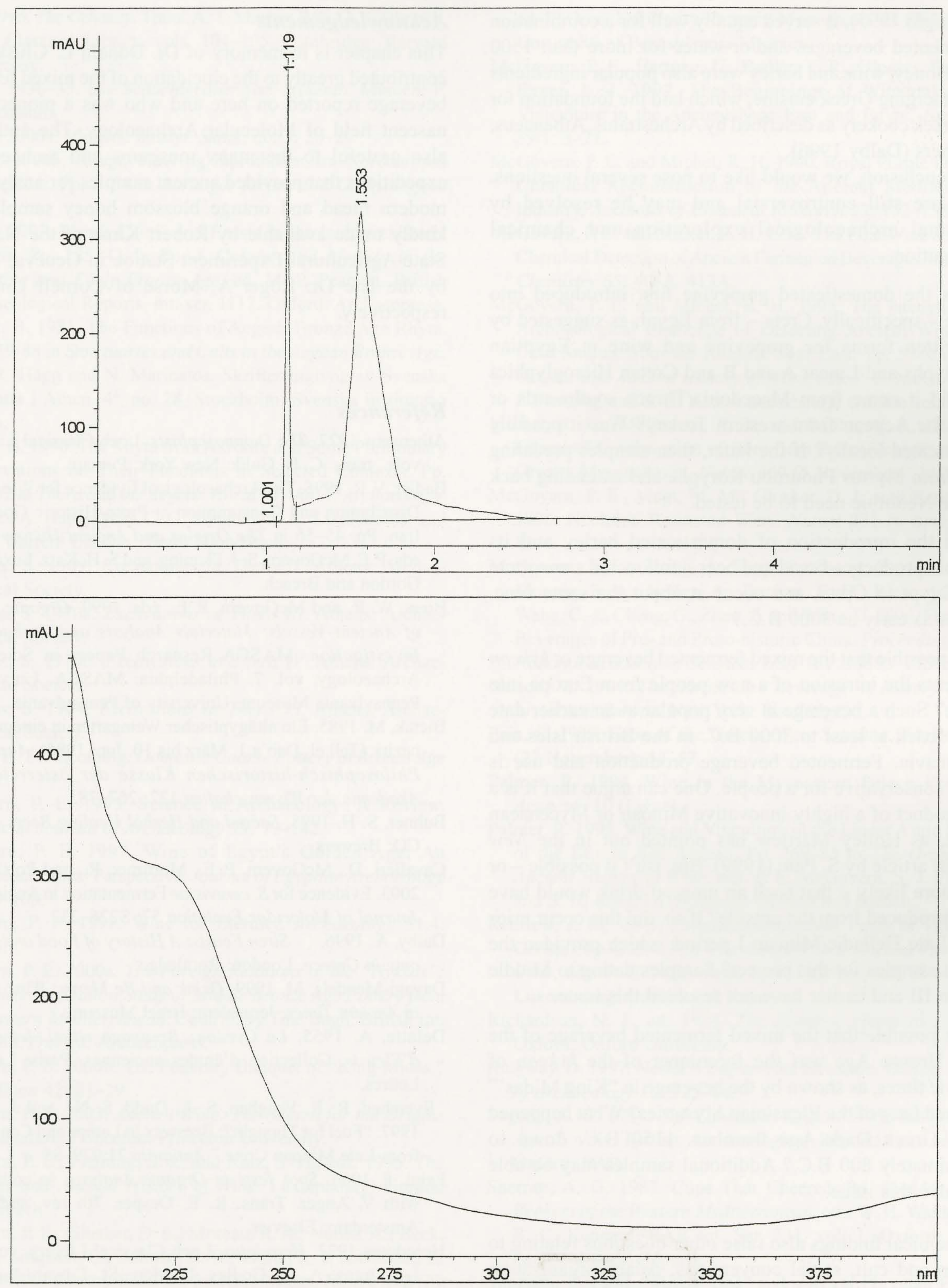

Figure 32 *Armenoi (EUM 122): liquid chromatogram and UV absorption spectrum at 1.56 min*

(see Wright 1995), it served equally well for a combination of fermented beverages and/or water for more than 1500 years. Honey, wine and barley were also popular ingredients in an emerging Greek cuisine, which laid the foundation for later Greek cookery as described by Archestratus, Athenaeus, and others (Dalby 1996).

In conclusion, we would like to pose several questions, which are still controversial and may be resolved by additional archaeological exploration and chemical investigation.

1) Was the domesticated grapevine first introduced into Greece – specifically, Crete – from Egypt, as suggested by the written forms for grapevine and wine in Egyptian hieroglyphs and Linear A and B and Cretan Hieroglyphics – or did it come from Macedonia/Thrace southwards or across the Aegean from western Turkey? Was it possibly domesticated locally? If the latter, then samples predating those from Myrtos Phournou Koryphe and extending back into the Neolithic need to be tested.

2) Did the introduction of domesticated barley and its principal products – bread and beer – follow the same route from Egypt to Crete, and occur at about the same time, perhaps as early as 3000 B.C.?

3) Is it possible that the mixed fermented beverage or *kykeon* represents the intrusion of a new people from Europe into Greece? Such a beverage is very popular at an earlier date there – back at least to 3000 B.C. in the British Isles and Scandinavia. Fermented beverage production and use is highly conservative for a people. One can argue that it is a new product of a highly innovative Minoan or Mycenaean culture, as Holley Martlew has pointed out in the *New Scientist* article by S. Pain (1999). But, isn't it possible – or even more likely – that such an unusual drink would have been introduced from the outside? If so, did this occur prior to the Late Helladic/Minoan I period, which provided the earliest samples for this project? Samples dating to Middle Minoan III and earlier have not resolved this issue.

4) Is it possible that the mixed fermented beverage of the Greek Bronze Age was the forerunner of the *kykeon* of Homeric times, as shown by the beverage in "King Midas'" tomb and later of the Eleusinian Mysteries? What happened in the Greek Dark Age from ca. 1150 B.C. down to approximately 800 B.C.? Additional samples may be able to resolve this issue.

The chemical findings also raise other questions relating to religion and cult, social conventions, palace organization and the economy, whose formulation is best left to specialists in the archaeology and history of Greece.

Acknowledgements

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References

Athenaeus 1927. *The Deipnosophists*. Loeb Classical Library, 10 vols., trans. C. B. Gulik. New York: Putnam.

Badler, V. R. 1995. The Archaeological Evidence for Winemaking, Distribution and Consumption at Proto-Historic Godin Tepe, Iran. Pp. 45–56 in *The Origins and Ancient History of Wine*, eds. P. E. McGovern, S. J. Fleming, and S. H. Katz. Luxembourg: Gordon and Breach.

Biers, W. R. and McGovern, P. E., eds. 1990. *Organic Contents of Ancient Vessels: Materials Analysis and Archaeological Investigation*. MASCA Research Papers in Science and Archaeology, vol. 7. Philadelphia: MASCA, University of Pennsylvania Museum, University of Pennsylvania.

Bietak, M. 1985. Ein altägyptischer Weingarten in einem Tempelbezirk (Tell el_Dab`a 1. März bis 10. Juni 1985). *Anzeiger der Philosophisch-historischen Klasse der österreichischen Akademie der Wissenschaften* 122: 267–78.

Buhner, S. H. 1998. *Sacred and Herbal Healing Beers*. Boulder, CO: Brewers.

Cavalieri, D., McGovern, P. E., Mortimer, R., and Polsinelli, M. 2003. Evidence for *S. cerevisiae* Fermentation in Ancient Wine. *Journal of Molecular Evolution* 57: S226–232.

Dalby, A. 1996. *Siren Feasts: A History of Food and Gastronomy in Greece*. London: Routledge.

Dayagi-Mendels, M. 1999. *Drink and Be Merry: Wine and Beer in Ancient Times*. Jerusalem: Israel Museum.

Delatte, A. 1955. *Le Cycéon: Breuvage rituel des Mystères d'Eleusis*. Collection d'études anciennes. Paris: Les Belles Lettres.

Evershed, R. P., Vaughan, S. J., Dudd, S. N. and J. S. Soles, 1997. "Fuel for Thought?: Beeswax in Lamps and Conical Cups from Late Minoan Crete." *Antiquity* 71:979–85.

Feigl, F. 1966. *Spot Tests in Organic Analysis*. In collaboration with V. Anger. Trans. R. E. Oesper. 7th rev. and enl. ed. Amsterdam: Elsevier.

Herodotus 1922. *Herodotus*. Loeb Classical Library, vol. 3, bks. I–II, trans. A. D. Godley. London: St. Edwardsburg; 1990 reprint.

Homer 1961. *The Iliad*. Trans. R. Lattimore. Chicago: University of Chicago.

Homer 1995. *The Odyssey*. Trans. A. T. Murray. Rev. G. E. Dimock. Loeb Classical Library, vols. 104–105. Cambridge: Harvard University.

Karo, G. 1930–33. *Die Schachtgräber von Mykenai*. Munich: F. Bruckmann.

Koch, E. 2000a. Vingede husdyr. *Skalk*, no. 3: 20–29.

Koch, E. 2000b, Bijagt, biavl og biprodukter fra Nordeuropas bronzealder. Pp. 7–54 in *Aarbøger for nordisk Oldkyndighed og*.

Koch, E. 2003. Mead, Chiefs and Feasts in the later prehistoric Europa. Pp. 125–43 in *Food, Culture and Identity in the Neolithic and Early Bronze Age*, ed. M. P. Pearson. British Archaeological Reports, int. ser. 1117. Oxford: Archaeopress.

Koehl, R. B. 1981. The Functions of Aegean Bronze Age Rhyta. Pp. 179-88 in *Sanctuaries and Cults in the Aegean Bronze Age*, eds. R. Hägg and N. Marinatos. Skrifter utgivna av Svenska institutet i Athen, 4°, no. 28. Stockholm: Svenska institutet i Athen.

Koehl, R. B. 1990. The Rhyta from Akrotire and Some Preliminary Observations on Their Functions in Selected Contexts. Pp. 350–62 in *Thera and the Aegean World III*. Vol. 1: *Archaeology*. Eds. D. A. Hardy, with C. G. Doumas, J. A. Sakellarakis, and P. M. Warren. London: Thera Foundation.

Marinatos, S. 1969. *Excavations at Thera II*. Athens: Archaeological Society.

Marinatos, S. 1970a. *Excavations at Thera III*. Athens: Archaeological Society.

Marinatos, S. 1970b. *Excavations at Thera IV*. Athens: Archaeological Society.

Marinatos, S. 1974. *Excavations at Thera VI*. Athens: Archaeological Society.

Martlew, H. Forthcoming. *Domestic Coarse Pottery in Bronze Age Crete*.

McGovern, P. E. 1995. Science in Archaeology: A Review. *American Journal of Archaeology* 99: 79–142.

McGovern, P. E. 1997. Wine of Egypt's Golden Age: An Archaeochemical Perspective. *Journal of Egyptian Archaeology* 83: 69-108.

McGovern, P. E. 1998. Wine for Eternity. *Archaeology* 51.4: 28–34.

McGovern, P. E. 2000a. *The Foreign Relations of the "Hyksos": A Neutron Activation Study of Middle Bronze Age Pottery from the Eastern Mediterranean*. Contrib. by Tine Bagh. British Int. Ser. 888. Oxford: Archaeopress.

McGovern, P. E. 2000b. The Funerary Banquet of "King Midas." *Expedition* 42: 21–29.

McGovern, P. E. 2003. *Ancient Wine: The Search for the Origins of Viniculture*. Princeton: Princeton University.

McGovern, P. E., Fleming, S. J., and Katz, S. H., eds. 1995. *The Origins and Ancient History of Wine*. Luxembourg: Gordon and Breach.

McGovern, P. E., Glusker, D. L., Moreau, R. A., Nuñez, A., Beck, C. W., Simpson, E., Butrym, E. D., Exner, L. J. and Stout, E. C. 1999. A Funerary Feast Fit for King Midas. *Nature* 402 (23 December): 863–864.

McGovern, P. E., and Harbottle, G. 1997. "Hyksos" Trade Connections between Tell el-Dab`a (Avaris) and the Levant: A Neutron Activation Study of the Canaanite Jar. Pp. 141–57 in *The Hyksos: New Historical and Archaeological Perspectives*, ed. E. Oren. University Museum Monograph 96. Philadelphia: University of Pennsylvania Museum.

McGovern, P. E., Hartung, U., Badler, V. R., Glusker, D. L. and Exner, L. J. 1997. The Beginnings of Winemaking and Viniculture in the Ancient Near East and Egypt. *Expedition* 39/1: 3–21.

McGovern, P. E. and Michel, R. H. 1990. Royal Purple Dye: The Chemical Reconstruction of the Ancient Mediterranean Industry. *Accounts of Chemical Research* 23: 152–158.

McGovern, P. E. and Michel, R. H. 1993. The First Wine and Beer: Chemical Detection of Ancient Fermented Beverages. *Analytical Chemistry* 65: 408A–413A.

McGovern, P. E. and Michel, R. H. 1995. The Analytical and Archaeological Challenge of Detecting Ancient Wine: Two Case Studies from the Ancient Near East. Pp. 57–65 in *The Origins and Ancient History of Wine*, eds. P. E. McGovern, S. J. Fleming, and S. H. Katz. Luxembourg: Gordon and Breach.

Michel, R. H., McGovern, P. E., and Badler, V. R. 1992. The Chemical Confirmation of Beer from Proto-Historic Lowland Greater Mesopotamia. *Nature* 360 (5 November): 24.

McGovern, P. E., Voigt, M. M., Glusker, D. L. and Exner, L. J. 1996. Neolithic Resinated Wine. *Nature* 381 (6 June): 480–81.

McGovern, P. E., Zhang, J., Tang, J., Zhang, Z., Hall, G. R., Moreau, R. A., Nuñez, A., Butrym, E. D., Richards, M. P., Wang, C.-s., Cheng, G., Zhao, Z. and Wang, C. 2004. Fermented Beverages of Pre- and Proto-historic China. *Proceedings of the National Academy of Sciences USA* 101: 17593–17598.

Nelson, M. 2004. *The Barbarian's Beverage: A History of Beer in Ancient Europe*. New York: Routledge.

Pain, S. 1999. Grog of the Greeks. *New Scientist* 164, no. 2214 (27 November): 54–57.

Palmer, R. 1994. Wine in the Mycenaean Palace Economy. *Aegaeum* 10 (Liège).

Palmer, R. 1995. Wine and Viticulture in the Linear A and B Texts of the Bronze Age Aegean. Pp. 269–85 in *The Origins and Ancient History of Wine*, eds. P. E. McGovern, S. J. Fleming, and S. H. Katz. Luxembourg: Gordon and Breach.

Renfrew, J. M. 1995. Palaeoethnobotanical Finds of *Vitis* from Greece. Pp. 255–67 in *The Origins and Ancient History of Wine*, eds. P. E. McGovern, S. J. Fleming, and S. H. Katz. Luxembourg: Gordon and Breach.

Richardson, N. J., ed. 1974. *The Homeric Hymn to Demeter.* Oxford: Oxford University.

Ridgway, D. 1997. Nestor's Cup and the Etruscans. *Oxford Journal of Archaeology* 16: 325–44.

Sagona, A. G. 1984. *The Caucasian Region in the Early Bronze Age*. 3 vols. British Archaeological Reports, int. ser. 214. Oxford: BAR.

Sherratt, A. G. 1987. Cups That Cheered. Pp. 81–114 in *Bell Beakers of the Western Mediterranean*, eds. W. H. Waldren and R. C. Kennard. BAR Int. Ser. 331, vol. 1. Oxford: British Archaeological Reports.

Simpson, E. 1990. "Midas' Bed" and a Royal Phrygian Funeral. *Journal of Field Archaeology* 17: 69–87.

Taylour, W. L. 1983. *The Mycenaeans*. Rev. ed. Ancient Peoples and Places, 39. London : Thames and Hudson.

Tubb, J. N. 1982. A Syrian "Klepsydra" of the Third Millennium B.C. *Levant* 14: 175–77.

Tzedakis, Y. and Martlew, H., eds. 1999. *Minoans and Mycenaeans: Flavours of Their Time*. Athens: Greek Ministry of Culture and National Archaeological Museum.

Warren, P. 1972. *Myrtos: An Early Bronze Age Settlement in Crete*. British School of Archaeology at Athens, suppl. vol. 7. London: Thames and Hudson for the British School of Archaeology at Athens.

Wiener, M. H. 1984. Crete and the Cyclades in LM I: The Tale of the Conical Cups. Pp. 17–26 in *The Minoan Thalassocracy: Myth and Reality*, eds. R. Hägg and N. Marinatos. Skrifter utgivna av Svenska institutet i Athen, 4°, no. 32. Stockholm: Svenska institutet i Athen.

Wiener, M. H. 1990. The Isles of Crete: The Minoan Thalassocracy Revisited. Pp. 128–60 in *Thera and the Aegean World III*. Vol. 1: *Archaeology*. Eds. D. A. Hardy, with C. G. Doumas, J. A. Sakellarakis, and P. M. Warren. London: Thera Foundation.

Wright, J. C. 1995. Empty Cups and Empty Jugs: The Social Role of Wine in Minoan and Mycenaean Societies. Pp. 287-309 in *The Origins and Ancient History of Wine*, eds. P. E. McGovern, S. J. Fleming, and S. H. Katz. Luxembourg: Gordon and Breach.

Young, R. S. 1981. *Three Great Early Tumuli*. The Gordion Excavation Final Reports, vol. 1. University Museum Monograph 43. Philadelphia: University Museum.

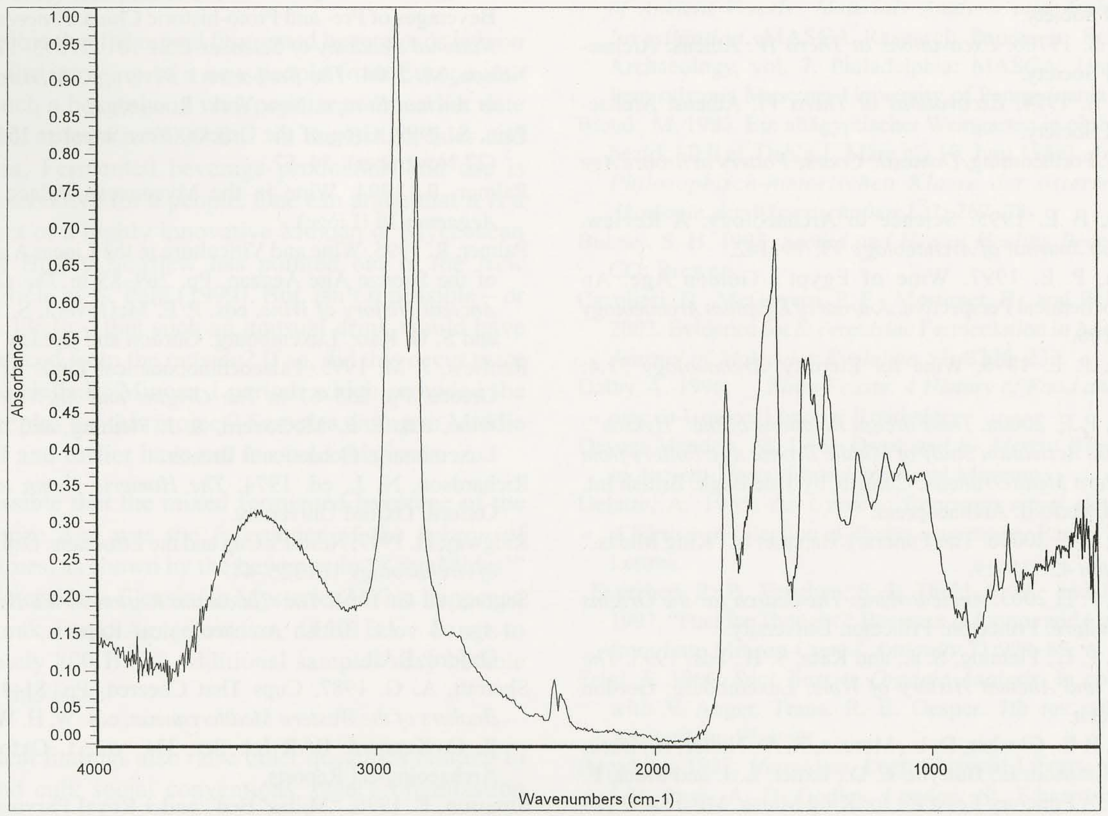

Figure 33 *Mycenae (EUM 67): infared spectrum*

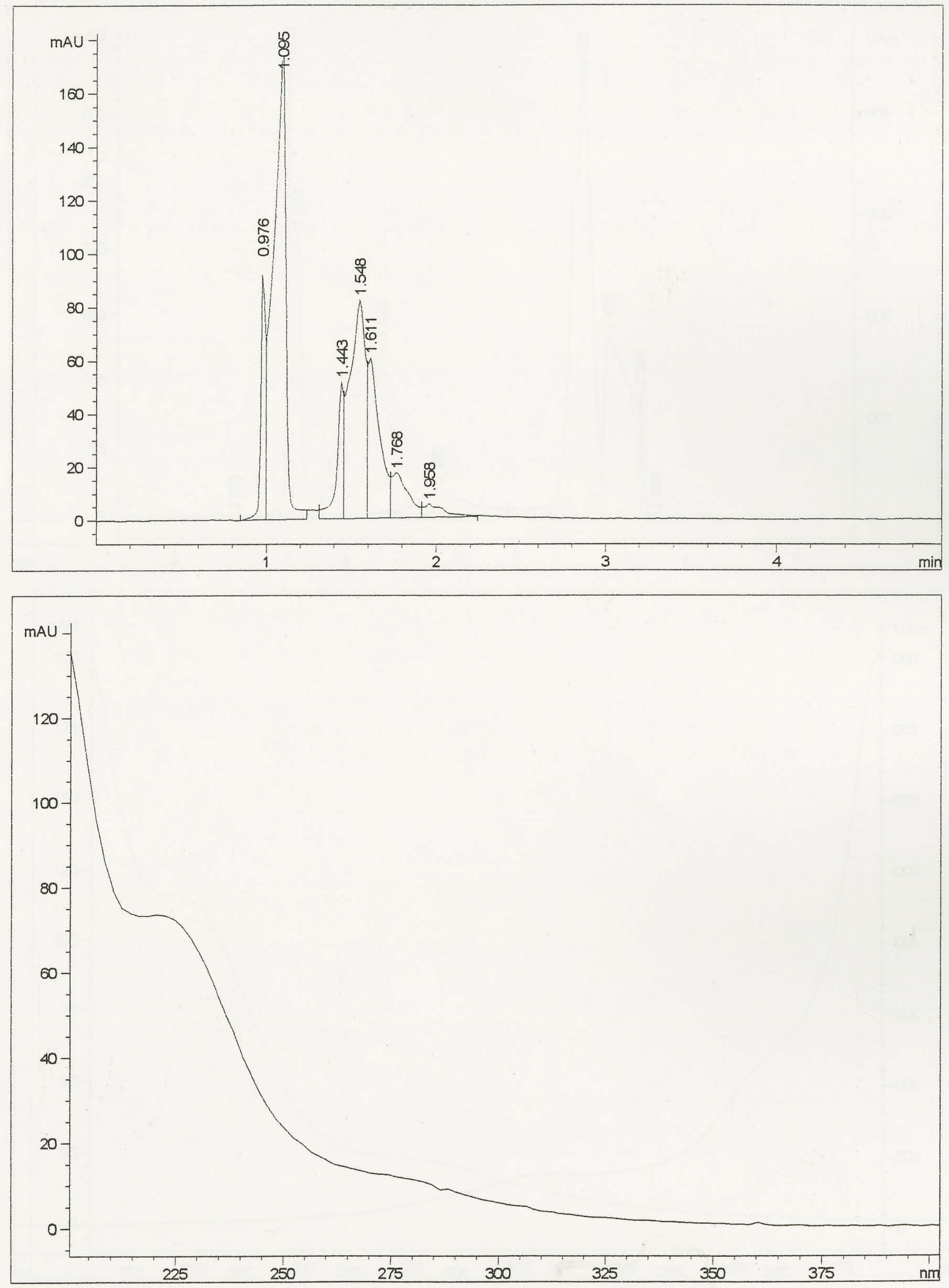

Figure 34 *Mycenae (EUM 67): liquid chromatogram and UV absorption spectrum at 1.55 min*

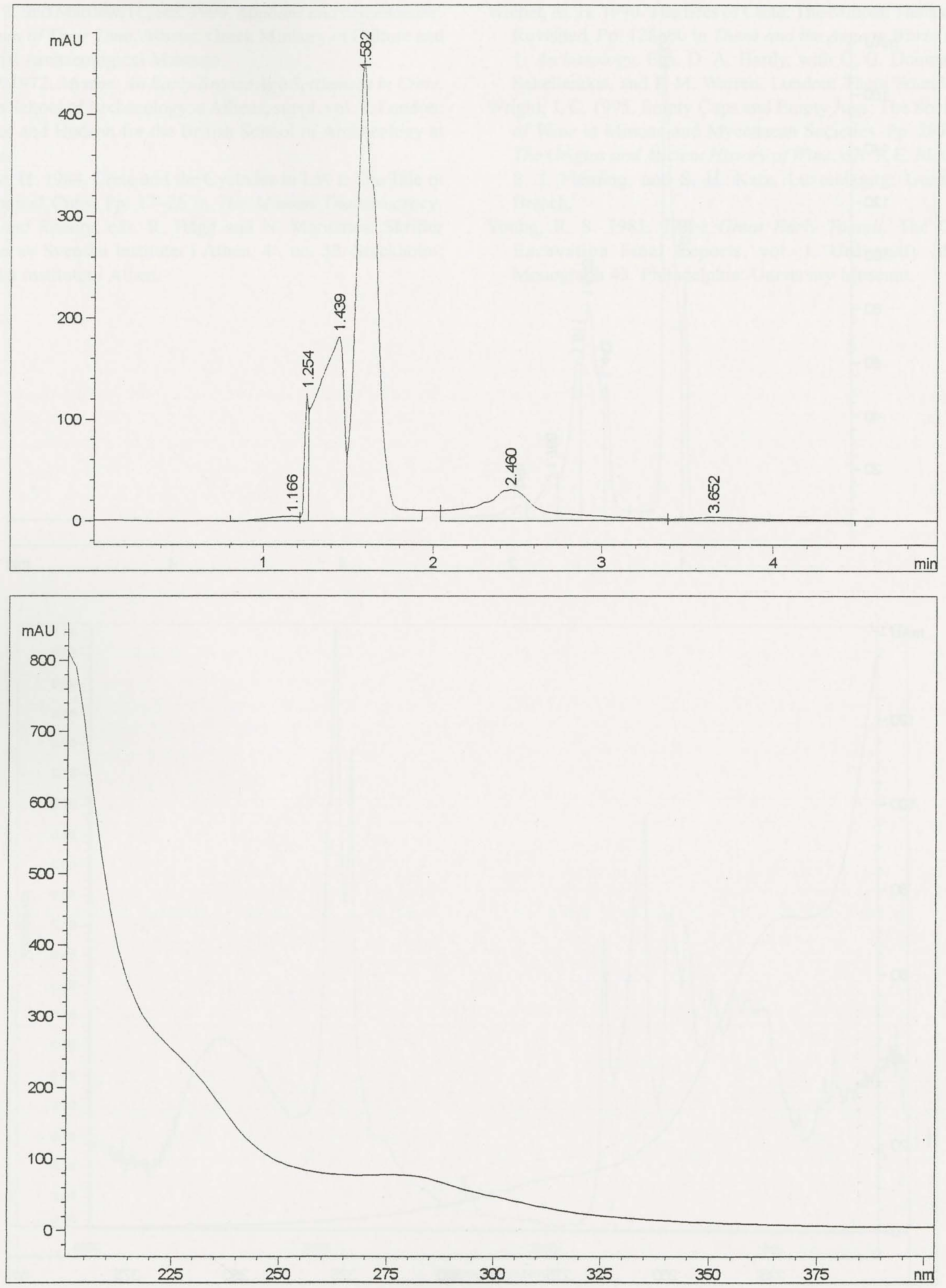

Figure 35 Mycenae (EUM 195): liquid chromatogram and UV absorption spectrum at 1.58 min

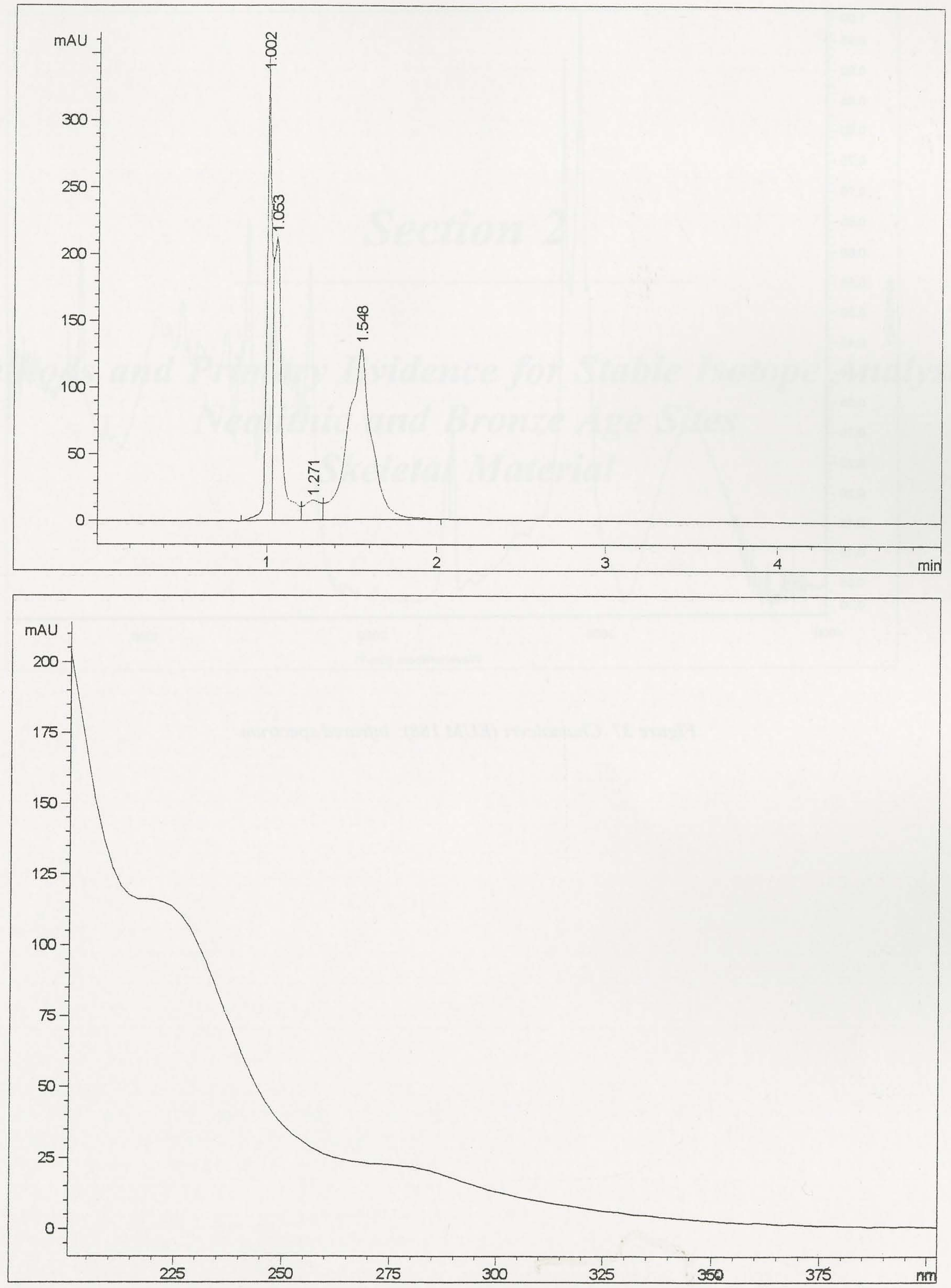

Figure 36 Chamalevri (EUM 180): liquid chromatogram and UV absorption spectrum at 1.55 min

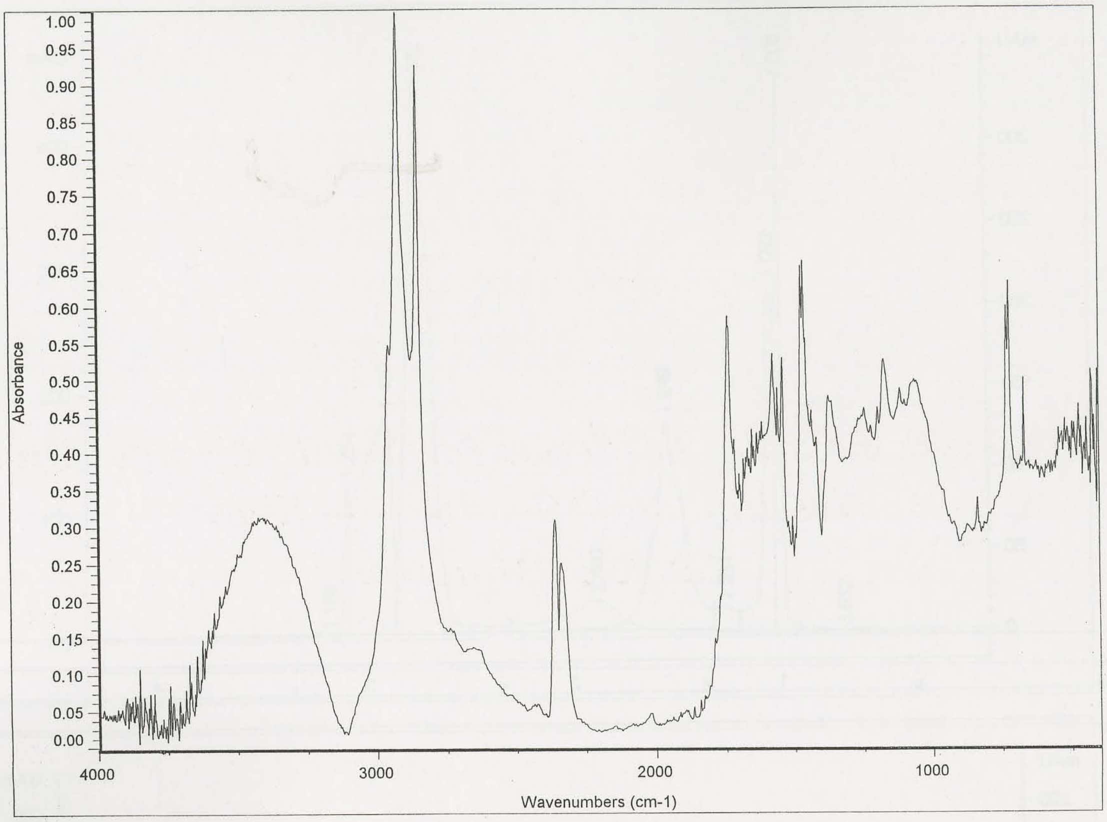

Figure 37 *Chamalevri (EUM 188): infrared spectrum*