Appendix V
Chemical analyses of copper alloy artefacts from Pyla-*Kokkinokremos* using portable X-Ray Fluorescence

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AV.1 Introduction

The excavations in 2010 and 2011 at the settlement of Pyla-*Kokkinokremos*, which uncovered a series of new rooms, brought to light a number of metallic artefacts made of copper alloys. They are described in detail in the catalogue of finds. In this Appendix we report on the results of the chemical analysis of these objects in an effort to shed some light into the practices of the smiths of the settlement, as well as identify the types of alloys used for the production of different artefacts.* Throughout the Early and Middle Bronze Age arsenical copper was the predominant alloy used by Cypriote smiths (Weinstein Balthazar 1990: 161), but by the Late Bronze Age arsenical copper is finally fully substituted by bronze, the alloy of copper and tin (Kassianidou 2003: 111). The two metals were mixed in different proportions in order to produce different types of objects. Sometimes lead was also added in order to increase the fluidity of the alloy (see below). Copper was locally available in the rich ore deposits located in the foothills of the Troodos mountains which were extensively exploited in the Late Bronze Age. Cypriote copper cast into oxhide ingots was produced in great quantities both for the local market and for export, as indicated by the discovery of ingots which according to Lead Isotope Analysis are consistent with a Cypriote provenance, in sites throughout the eastern and central Mediterranean (Kassianidou 2013; Gale 1999, 2011). Tin would have had to be imported to the island from a still unknown source, probably located somewhere in central Asia (Muhly 1999: 21; Pigott 2011: 276–281; Constantinou 2012: 7).

It is already well known that Pyla-*Kokkinokremos* was occupied for only a short period of time at the end of the 13th and the beginning of 12th century BC, namely at the end of the LC IIC period (Karageorghis & Demas 1984: 68; Georgiou 2012b: 68). This is believed to be a time of crisis throughout the eastern Mediterranean which, among other things, had greatly affected the trade of metals (Muhly 1992: 21). Although self-sufficient in copper, which was still being produced and cast into oxhide ingots up to the 11th century BC (Kassianidou 2013), Cyprus would also have been affected by this crisis, since the flow of tin would most probably have been disrupted. Thus it has been argued that the flourishing Cypriote metalworking industry of the 12th century BC may have largely relied on the systematic recycling of bronze artefacts (Karageorghis & Kassianidou 1999: 172). Support for this idea is provided by the numerous excavated metal hoards dating to the 12th century BC which often include scrap metal (Knapp *et al*. 1988: 257), but also by the clear evidence of looting of earlier tombs from which metal artefacts were systematically collected and removed (Karageorghis & Kassianidou 1999: 172; Sherratt 2012: 158).

Thus the analysis of the copper alloy objects from an archaeologically and chronologically well-defined context which falls within these 'Crisis Years', such as the assemblage from Pyla *Kokkinokremos*, is significant. Although metal artefacts were also found in the 1981–1982 excavation (Karageorghis & Demas 1984: 55–58), only a few were chemically analysed, using a variety of techniques (Gale & Stos-Gale 1984: 96).

* The analyses of the objects were carried out as part of a post-doctoral research project entitled 'A Diachronic Study of Cypriot Metalwork' undertaken by Andreas Charalambous. This is part of the NARNIA (New Archaeological Research Network for Integrating Approaches to Ancient Material Studies) Project that is coordinated by Vasiliki Kassianidou. NARNIA is a Marie Curie Initial Training Network which is funded by the FP7 and the European Union (for more information visit the NARNIA website: http://narnia-itn.eu/). The authors would like to thank Professor Vassos Karageorghis, Dr Athanasia Kanta and Dr Artemis Georgiou for their collaboration and assistance in the study of this material. Also we would like to thank Dr Giorgos Papasavvas for his valuable review of the manuscript.

The only copper based artefacts that Gale and Stos-Gale included in their study were two fragments of copper oxhide ingots and a fragment of a slab ingot, the chemical composition of which was determined by electron microprobe analysis (Gale & Stos-Gale 1984: 100, 103).

For the present study, a total of 65 copper alloy objects were analysed. Over half of the assemblage consists of scrap metal (**Fig. AV.1**), either in the form of droplets (P.N.127.11, P.N.127.12) (**Fig. AV.1a**), wire in a variety of thicknesses (P.N.34, P.N.128.1) (**Fig. AV.1b**), small amorphous lumps (P.N.127.10, P.N.127.24) (**Fig. AV.1c**), thin, irregular masses (P.N.35, P.N.39, P.N.40, P.N.42, P.N.44, P.N.118, P.N.125, P.N.127.6, P.N.127.18, P.N.127.27, P.N.127.28, P.N.127.29, P.N.130) (**Fig. AV.1d**), and sheet metal (P.N.41, P.N.122, P.N.123, P.N. 127.8, P.N.127.13, P.N.127.31B, P.N.127.32, P.N.128.2, P.N.129, P.N.130, P.N.131) (**Fig. AV.1e**). The sheets are quite different from the thin masses of metal. The former are deliberate artefacts, namely metal which has been hammered to form a thin, flat surface, and some of them are folded or twisted. The latter are usually small and irregular pieces which may have been accidentally formed either within crucibles or by spillages of metal. These pieces, together with the droplets and the amorphous lumps, may be the remains of casting activities.

There is also another different category of scrap metal, namely a number of fragmentary artefacts which seem to have been deliberately broken in order to be recycled (**Fig. AV.2**). Some may actually have been damaged and then disposed of. They include tools such as needles (P.N.127.15, P.N.127.17, P.N.128.3), a drill (P.N.127.9), the perforated butt of a small flat tool (P.N.127.23), perhaps a handle (P.N.127.21), weapons such as spearheads (P.N.127.4, P.N.127.19) (**Fig. AV.2a**) and a dagger (P.N.128.4) (**Fig. AV.2b**), and ornaments such as a fibula (P.N.127.14) and an earring (P.N.127.16). Among them, a bull figurine which has been cut in half (P.N.121) (**Fig. AV.2c**) stands out, as does an extraordinary petal-shaped bronze attachment decorated in relief on one side (P.N.45). Two small triangular flat pieces (P.N.127.25 and P.N.127.126) may be the 'handles' of miniature oxhide ingots such as the ones known from Enkomi and elsewhere (Giumlia-Mair *et al*. 2011; Papasavvas 2009: 101–104).

Some pieces (for example P.N.127.31A, P.N.127.31C and P.N.127.31D) have been cut so small that it is not easy to identify the original object. Perhaps an exception is the small cylindrical fragment (P.N.127.7) with a diameter of 0.5cm, which, based on its chemical composition (see below), we suggest may in fact be a piece of a rod tripod stand.

There are but a few complete (or almost complete) objects, such needles and/or pins (P.N.36, P.N.37, P.N.124, P.N.126, P.N.127.22), a bracelet (P.N.127.1), a pendant in the shape of a flower or pomegranate

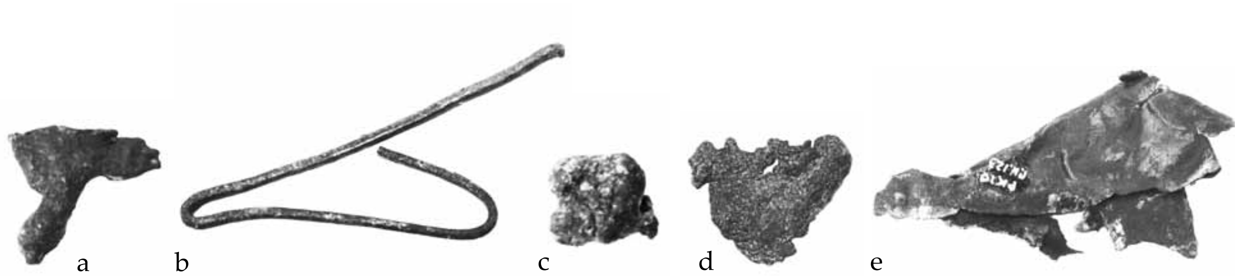

Figure AV.1. Scrap metal a. droplet (P.N.127.12), b. wire (P.N.128.1), c. amorphous lumps (P.N.127.10), d. thin irregular mass (P.N.35), e. sheet (P.N.123)

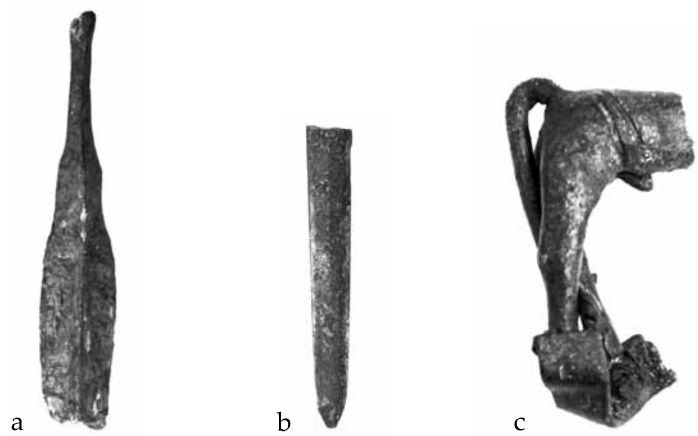

Figure AV.2. Scrap metal a. spearhead (P.N.127.4), b. dagger (P.N.128.4), c. broken bull figurine (P.N.121)

(P.N.127.2), which was perhaps part of the decoration of a four-sided stand or a rod tripod, such as the examples from Tiryns and Palaepaphos-*Skales* (Papasavvas 2001: 235, 237), an earring (P.N.127.3), a handle (P.N.127.5), a nail(?) (P.N.127.20) and a spatula (P.N.132). Some of them were part of a hoard (namely those with inventory P.N.127) that includes scrap metal and, therefore, it is most probable that they too must have been meant for recycling.

Seven fragments of copper slag were also recovered from one of the rooms (Room 32), where a small hoard of seven objects (those with an inventory number P.N.128) was also found. No metallurgical ceramics such as tuyères and crucibles have been recovered. The presence of metal scrap, together with the absence of significant quantities of slag, may act as an indicator for the presence of a metalworking workshop (rather than a metallurgical one) in the vicinity of the excavated area.

AV.2 Method of analysis

A search through the literature will reveal that most of the published chemical analyses of contemporary metal artefacts from Cyprus concern either copper oxhide ingots, or the waste products of metallurgical processes, namely the slag and the remains of smelting and casting installations. There are but a few on utilitarian objects such as tools and weapons, and even less on the masterpieces of the Late Cypriote smiths, such as the four-sided stands. This is not surprising: analytical techniques such as Atomic Absorption Spectroscopy or Inductively Coupled Plasma Spectroscopy, thought to be the most appropriate for metal analysis, cannot be used without sampling and museum curators are becoming more and more reluctant to allow sampling of ancient complete and even fragmentary artefacts (Giumlia-Mair *et al*. 2011: 11). The application of a portable handheld XRF allows the non-destructive analysis of metal artefacts and is becoming more and more popular, especially in analytical studies of metal objects made either of precious or base metals, where sampling is not permitted. X-ray Fluorescence (XRF) spectrometry is a well-known, non-destructive analytical method which can determine the chemical composition of an object without sampling or coming into contact with it (Lutz & Pernicka 1996; Karydas 2007; Frahm & Doonan 2013). However, if the object is covered by rough or thick patina, the upper layer should be carefully removed in a very small area in order to guarantee reliable results.

A portable handheld Innov-X Delta ED-XRF analyser (pXRF) was used to determine the chemical composition of all bronze artefacts examined here. The specific instrument, which belongs to the Archaeological Research Unit of the University of Cyprus, is equipped with a 4W, 50kV tantalum anode X-Ray tube and a high performance Silicon Drift Detector (SDD). The X-rays are emitted by a miniaturised X-ray tube, located in the interior of the instrument, behind a prolene film window. The diameter of the X-Ray beam, adjusted by the use of a collimation coin, is smaller than 3mm (~2.5mm). The measurement time for each spot analysis was 70 seconds. The final measurement value for each analysed object is the mean value of three to five measurements conducted on corrosion-free areas of each object.

The analytical mode of the instrument employed for the analyses of these objects is Alloy Plus. For this mode, Beam 1 (40kV) analyses the elements Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Hf, Ta, W, Re, Pt, Au, Pb, Bi, Zr, Nb, Mo, LE (light elements), Pd, Ag, Sn and Sb, while Beam 2 (10kV) is used for the determination of Mg, Al, Si, P and S. In order to determine the concentration of arsenic (As), the objects were also analysed using the Mining mode of the instrument. The analytical data and other information concerning the experimental conditions were exported into an Excel spread sheet for further mathematical treatment. Alloy analysis utilises a Fundamental Parameters algorithm to determine elemental concentration. This method calculates chemistry from the spectral data, without the requirement of stored fingerprints. Also, for checking the accuracy of the Alloy Plus and the Mining (for the case of As) modes, standard reference materials (SRMs) like CRM-875 (bronze standard) and BCR-691 (set of five copper alloys) were used.

A high resolution handheld microscope (ProScope HR, Bodelin Technologies) was used to study in detail the artefacts' surfaces and to detect areas free of corrosion suitable to be used for the ED-XRF analyses (**Fig. AV.3**).

AV.3 Results

The results of the compositional analysis are presented in **Table AV.1**. They show that the greatest majority of the 65 studied objects from Pyla-*Kokkinokremos* are bronzes with a varied ratio of copper to tin. **Figure AV.4** is a histogram depicting the concentration of

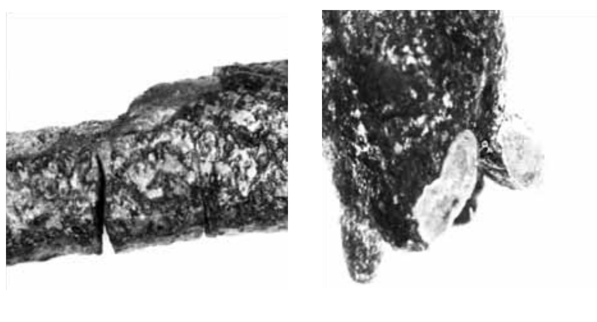

Figure AV.3. Images of clean surfaces of two artefacts, taken by the handheld digital microscope

Sample	**Artefact**	**Composition (wt% ± std)**					
		Cu	Sn	Pb	As	Fe	Zn
P.N. 34	Wire	96 ± 0.6	3.2 ± 0.4	0.2 ± 0.03	n.d	0.6 ± 0.1	n.d
P.N. 35	Scrap metal/ thin mass	95.9 ± 0.5	3.8 ± 0.4	n.d	n.d	0.3 ± 0.05	n.d
P.N. 36	Needle	94 ± 0.6	5.2 ± 0.5	0.1 ± 0.03	n.d	0.7 ± 0.1	n.d
P.N. 37	Needle/pin	93 ± 0.5	6.1 ± 0.4	n.d	0.05 ± 0.01	0.6 ± 0.1	n.d
P.N. 39	Scrap metal/ thin mass	93.6 ± 0.4	5.3 ± 0.2	0.4 ± 0.03	0.04 ± 0.01	0.6 ± 0.1	n.d
P.N. 40	Scrap metal/ thin mass	89.9 ± 0.8	9.5 ± 0.6	n.d	0.1 ± 0.03	0.5 ± 0.1	n.d
P.N. 41	Scrap metal/ sheet	98 ± 0.3	1.5 ± 0.2	n.d	n.d	0.5 ± 0.1	n.d
P.N. 42	Scrap metal/ thin mass	94.7 ± 0.6	5 ± 0.3	n.d	0.1 ± 0.2	0.2 ± 0.04	n.d
P.N. 44	Scrap metal/ thin mass	85.6 ± 0.7	13.8 ± 0.5	0.05 ± 0.01	0.2 ± 0.03	0.4 ± 0.1	n.d
P.N. 45	Attachment	96 ± 0.3	3.6 ± 0.2	0.05 ± 0.01	n.d	0.3 ± 0.04	n.d
P.N. 118	Scrap metal/ thin mass	85.6 ± 0.7	13.3 ± 0.6	n.d	0.2 ± 0.03	0.5 ± 0.04	0.4 ± 0.03
P.N. 121	Bull figurine	87.4 ± 0.9	11.3 ± 0.7	0.06 ± 0.01	0.2 ± 0.02	0.6 ± 0.1	0.4 ± 0.03
P.N. 122	Scrap metal/ sheet	92.9 ± 0.4	6.4 ± 0.3	n.d	0.2 ± 0.02	0.3 ± 0.04	0.2 ± 0.02
P.N. 123	Scrap metal/ sheet	86.9 ± 0.6	12.6 ± 0.5	n.d	0.1 ± 0.02	0.2 ± 0.02	0.2 ± 0.03
P.N. 124	Needle	88.1 ± 0.7	10.1 ± 0.4	0.1 ± 0.02	0.2 ± 0.03	1.5 ± 0.2	n.d
P.N. 125	Scrap metal/ thin mass	93.9 ± 0.3	5.2 ± 0.2	0.05 ± 0.01	0.5 ± 0.04	0.3 ± 0.02	n.d
P.N. 126	Needle	88.5 ± 0.9	10.5 ± 0.6	n.d	0.05 ± 0.01	0.9 ± 0.2	n.d
P.N. 127.1	Bracelet	93.5 ± 0.5	6.3 ± 0.4	n.d	n.d	0.2 ± 0.03	n.d
P.N. 127.2	Pendant	88.7 ± 1	7.7 ± 0.4	1 ± 0.2	0.05 ± 0.01	2.5 ± 0.3	n.d
P.N. 127.3	Earring	95.2 ± 0.3	4.5 ± 0.2	n.d	n.d	0.3 ± 0.03	n.d
P.N. 127.4	Spearhead	94.3 ± 0.7	5.2 ± 0.6	0.05 ± 0.01	0.3 ± 0.04	0.15 ± 0.02	n.d
P.N. 127.5	Handle of a lid	97.5 ± 0.5	2.3 ± 0.4	n.d	0.05 ± 0.01	0.1 ± 0.03	n.d
P.N. 127.6	Scrap metal/ thin mass	91.4 ± 0.8	8.2 ± 0.5	n.d	0.1 ± 0.2	0.3 ± 0.04	n.d
P.N. 127.7	Scrap metal	73 ± 1.1	5.9 ± 0.4	19.9 ± 0.6	n.d	1.2 ± 0.1	n.d
P.N. 127.8	Scrap metal/ sheet	94 ± 0.6	5.4 ± 0.5	n.d	0.08 ± 0.02	0.5 ± 0.04	n.d
P.N. 127.9	Tool/drill(?)	96.4 ± 0.4	3.2 ± 0.3	n.d	n.d	0.2 ± 0.03	n.d
P.N. 127.10	Scrap metal/ lump	98.7 ± 0.3	0.5 ± 0.1	n.d	0.2 ± 0.03	0.5 ± 0.1	0.1 ± 0.02
P.N. 127.11	Scrap metal/ droplet	95.2 ± 0.4	4.1 ± 0.2	n.d	n.d	0.5 ± 0.1	0.2 ± 0.03
P.N. 127.12	Scrap metal/ droplet	97.1 ± 0.5	2 ± 0.3	n.d	0.1 ± 0.02	0.5 ± 0.1	0.2 ± 0.02
P.N. 127.13	Scrap metal/ sheet	98.7 ± 0.03	0.5 ± 0.1	n.d	0.1 ± 0.02	0.5 ± 0.1	0.2 ± 0.02
P.N. 127.14	Fibula(?)	95.9 ± 0.4	3.8 ± 0.3	n.d	0.05 ± 0.01	0.2 ± 0.03	n.d
P.N. 127.15	Needle	97.3 ± 0.3	2.3 ± 0.2	n.d	0.05 ± 0.01	0.3 ± 0.04	n.d

Table AV.1. Results of the compositional analysis

P.N. 127.16	Earring(?)	97.2 ± 0.3	2.5 ± 0.2	n.d	n.d	0.2 ± 0.02	n.d
P.N. 127.17	Needle	97.1 ± 0.4	2.6 ± 0.3	n.d	0.05 ± 0.01	0.2 ± 0.03	n.d
P.N. 127.18	Scrap metal/ thin mass	94.3 ± 0.4	5 ± 0.3	0.25 ± 0.02	0.05 ± 0.01	0.2 ± 0.03	0.2 ± 0.03
P.N. 127.19	Spearhead	96.4 ± 0.3	3.3 ± 0.2	n.d	0.05 ± 0.01	0.2 ± 0.04	n.d
P.N. 127.20	Nail(?)	98.9 ± 0.3	n.d	n.d	0.1 ± 0.02	0.9 ± 0.2	0.1 ± 0.02
P.N. 127.21	Handle(?) (fragment)	94.1 ± 0.6	5.4 ± 0.5	n.d	0.1 ± 0.02	0.35 ± 0.05	n.d
P.N. 127.22	Needle/pin(?)	97.2 ± 0.4	2.5 ± 0.3	n.d	0.05 ± 0.01	0.2 ± 0.03	n.d
P.N. 127.23	Tool(?)	91.1 ± 0.5	5.3 ± 0.2	3.2 ± 0.2	0.1 ± 0.02	0.3 ± 0.04	n.d
P.N. 127.24	Scrap metal/ lump	95.2 ± 0.3	4.2 ± 0.2	0.25 ± 0.03	n.d	0.3 ± 0.03	n.d
P.N. 127.25	Handle of miniature oxhide ingot(?)	95.6 ± 0.5	3.8 ± 0.4	n.d	0.1 ± 0.01	0.2 ± 0.04	0.25 ± 0.03
P.N. 127.26	Handle of miniature oxhide ingot(?)	98 ± 0.2	1.2 ± 0.1	0.2 ± 0.02	0.05 ± 0.01	0.3 ± 0.05	0.2 ± 0.02
P.N. 127.27	Scrap metal/ thin mass	98.4 ± 0.3	n.d	0.05 ± 0.01	0.45 ± 0.1	1.1 ± 0.1	n.d
P.N. 127.28	Scrap metal/ thin mass	96 ± 0.3	3.5 ± 0.2	n.d	0.05 ± 0.01	0.4 ± 0.05	n.d
P.N. 127.29	Scrap metal/ thin mass	96 ± 0.3	3.6 ± 0.2	n.d	0.05 ± 0.01	0.3 ± 0.04	n.d
P.N. 127.30	Scrap metal/ thin mass	89.6 ± 0.6	9.7 ± 0.5	n.d	0.05 ± 0.01	0.5 ± 0.07	0.1 ± 0.02
P.N. 127.31A	Scrap metal	95.8 ± 0.3	3.4 ± 0.2	n.d	0.1 ± 0.02	0.7 ± 0.1	n.d
P.N. 127.31B	Scrap metal/ sheet	95.7 ± 0.4	3.9 ± 0.3	n.d	0.08 ± 0.01	0.3 ± 0.03	n.d
P.N. 127.31C	Scrap metal	97 ± 0.3	2.3 ± 0.2	0.2 ± 0.02	0.1 ± 0.02	0.4 ± 0.03	n.d
P.N. 127.31D	Scrap metal	95.5 ± 0.4	4.1 ± 0.3	n.d	0.05 ± 0.01	0.3 ± 0.04	n.d
P.N. 127.32A	Scrap metal/ sheet	96.5 ± 0.5	3 ± 0.4	n.d	0.05 ± 0.01	0.4 ± 0.04	n.d
P.N. 127.32B	Scrap metal/ sheet	94.3 ± 0.7	4.9 ± 0.5	0.05 ± 0.01	0.2 ± 0.02	0.5 ± 0.1	n.d
P.N. 127.32C	Scrap metal/ sheet	97.2 ± 0.5	2 ± 0.3	0.1 ± 0.03	0.1 ± 0.02	0.6 ± 0.1	n.d
P.N. 128.1	Wire	93.1 ± 0.4	6.5 ± 0.3	n.d	0.08 ± 0.01	0.3 ± 0.04	n.d
P.N. 128.2A	Scrap metal/ sheet	88.5 ± 0.7	11.1 ± 0.6	0.05 ± 0.01	0.1 ± 0.02	0.2 ± 0.05	n.d
P.N. 128.2B	Scrap metal/ sheet	87.1 ± 0.6	12.7 ± 0.5	n.d	0.1 ± 0.03	0.1 ± 0.01	n.d
P.N. 128.3	Pin/needle(?)	84.5 ± 0.7	14.9 ± 0.5	n.d	0.1 ± 0.02	0.5 ± 0.1	n.d
P.N. 128.4A	Dagger	81.5 ± 0.8	16.8 ± 0.5	1.3 ± 0.2	0.3 ± 0.05	0.08 ± 0.02	n.d
P.N. 128.4B	Scrap metal/ sheet	93.2 ± 0.5	6.2 ± 0.4	0.3 ± 0.04	0.05 ± 0.01	0.2 ± 0.03	n.d
P.N. 128.5	Needle	88.9 ± 0.5	10.7 ± 0.4	n.d	0.05 ± 0.01	0.3 ± 0.04	n.d

Table AV.1. Results of the compositional analysis (continued)

P.N. 129	Scrap metal/ sheet	99.1 ± 0.2	n.d	0.05 ± 0.01	0.05 ± 0.01	0.7 ± 0.1	0.1 ± 0.02
P.N. 130	Scrap metal/ sheet	96.3 ± 0.3	3.4 ± 0.2	n.d	n.d	0.3 ± 0.05	n.d
P.N. 131	Scrap metal/ sheet	95.4 ± 0.3	4.4 ± 0.2	n.d	n.d	0.15 ± 0.02	n.d
P.N. 132	Spatula	88.9 ± 0.5	10.7 ± 0.4	n.d	0.05 ± 0.01	0.2 ± 0.04	0.1 ± 0.02

Table AV.1. Results of the compositional analysis (continued)

copper and **Figure AV.5** the concentration of tin in the analysed artefacts in weight per cent. The assemblage consists mostly of scrap metal and only a few finished or identifiable objects, which exhibit a great variability in the tin content. There does not even seem to be a consistent use of the same alloy for the same type of object. For example, the amount of tin in the alloys used to make needles ranges from 2.3 to 10.7%.

Only three artefacts, the nail (P.N.127.20) and two pieces of scrap (P.N.127.27 and P.N.129) contain no tin. Four objects have a tin concentration ranging between 0.5 and 1.5%. Because Cypriote copper ores are very 'clean', and thus contain no tin (Constantinou 1982: 15; Muhly 1985a: 277), even this small amount must have been added either deliberately or accidentally. The very low tin content in the specific four objects possibly indicates the melting together of copper metal with a quantity of bronze scrap, originally containing a higher amount of tin (Weinstein Balthazar 1990: 72–73) or perhaps the consecutive use of the same crucible to melt copper alloys of different compositions.

There are 27 artefacts with a tin concentration between 2 and 4.9%. The addition of tin improves the hardness and the corrosion resistance and decreases the melting temperature of the alloy (Klein & Hauptmann 1999; Figueiredo *et al*. 2010; Ashkenazi *et al*. 2012). Hall and Steadman (1991: 230, n. 2) have argued that anything less than 5% tin should be considered accidental rather than a deliberate addition, as this small amount does not significantly change either the melting point or the hardness of the alloy and, therefore, ancient smiths would not have been able to detect the presence of the tin, if, for example, they were melting together metal of different compositions. Moorey (1994: 252), however, has argued against this idea, since early Mesopotamian texts indicate that a wide range of alloys were being used including some which had a tin content below 3%.

Less than half of the assemblage has a tin concentration 5% or higher and out of these only 14 objects have a tin concentration higher than 9%. This latter group consists of four needles, a spatula, the bull figurine and the tip of a dagger, which was found to contain 16.8% tin. Only the spatula is an intact artefact, which may still have been used. All the others, together with the rest of the objects, were scrap metal.

As for the two hoards of objects, it is worth mentioning that all 37 analysed objects (127.1–127.32) of the hoard of room 41 have a tin content lower than 9.7%, while five of the seven objects (128.1–128.5) of the second hoard, found in room 32, have a tin content that is higher than 10.7%.

Two small fragments (P.N.127.25 and P.N.127.26) look like they could be the 'handles' of miniature oxhide ingots. Both of them contain tin: the first has 3.8% and the second 1.2%. The fact that the amount of tin is different means that the fragments come from

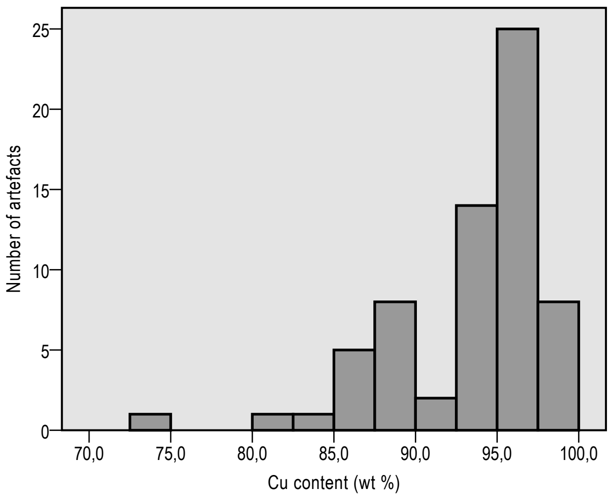

Figure AV.4. Histogram showing the concentration of copper (Cu) in the studied objects in weight %

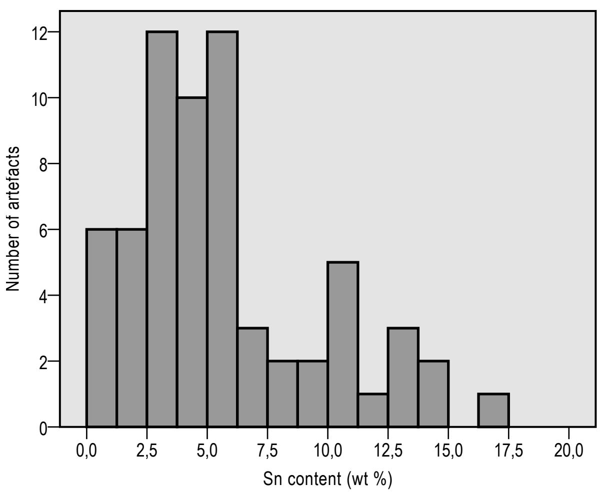

Figure AV.5. Histogram showing the concentration of tin (Sn) in the studied objects in weight %

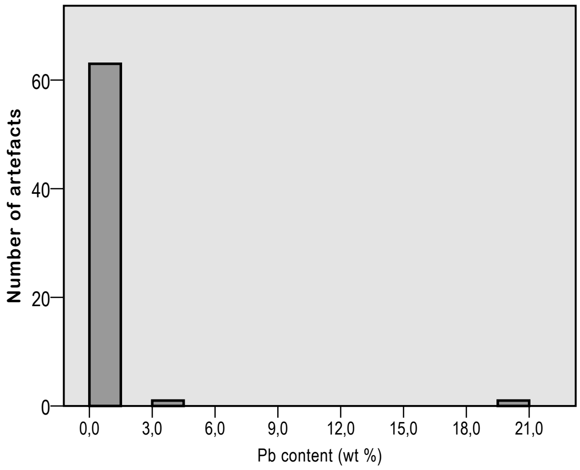

Figure AV.6. Histogram showing the concentration of lead (Pb) in the studied objects in weight %

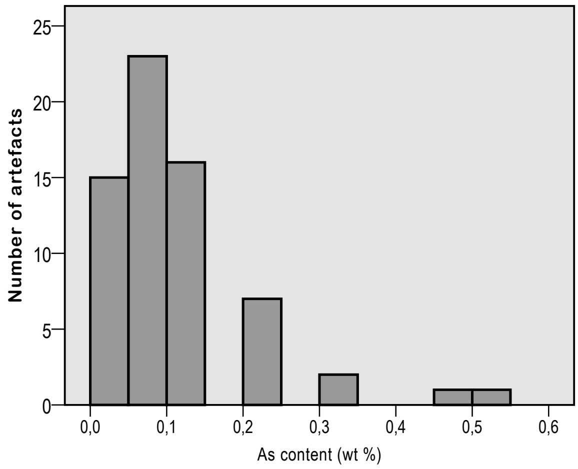

Figure AV.7. Histogram showing the concentration of arsenic (As) in the studied objects in weight %

two different objects. On the other hand, a recent investigation of miniature oxhide ingots from Enkomi and Mathiatis indicated that they were all made of pure copper (Giumlia-Mair *et al*. 2011: 16). Thus either these artefacts are not in fact fragments of miniature oxhide ingots, or perhaps not all miniature ingots were made of pure copper. Indeed, the miniature ingot from the Makarksa hoard, which Sherratt (2012: 158) has recently argued most probably consists of objects originating in Cyprus, is made of bronze.

Lead (Pb) is detected only in 23 objects, at levels ranging from 0.05 to 0.4%, while in four cases the amount of lead is much higher. **Figure AV.6** is a histogram depicting the concentration in weight per cent of lead in the studied bronze objects. The fact that lead, as tin, is not present in Cypriote copper ores (Constantinou 1982: 15) indicates a deliberate addition to the bronze objects, in order to improve fluidity and castability (Klein & Hauptmann 1999). The addition of only 2–3% lead is sufficient to produce the maximum increase in fluidity (Philip 1991) and also to lower the melting point of the alloy (Giumlia-Mair 1992). The lower concentration of lead, detected in the majority of the 23 objects, doesn't provide these advantages. Thus the presence of lead may again be the result of melting together copper with a quantity of scrap metal, which contained much higher amounts of the specific component (Muhly 1985b: 80). Furthermore, it should be noted that even such small additions of lead would greatly affect the Lead Isotope Analysis results (Gale & Stos-Gale 1985: 97). The technique is based on the assumption that the lead in the bronze originates in the copper ores and thus can identify the source of the copper (Gale & Stos Gale 1985: 87–88). Lead would have been imported to Cyprus either from Anatolia or from Laurion. Thus, for example, even if a very small amount of lead from Laurion was added to the melt, then the Lead Isotope Analysis would find that the copper was consistent with a Laurion provenance.

The objects with higher concentrations in lead are the pendant (P.N.127.2), the dagger (P.N.128.4A), a tool (P.N.123.23) and the small cylindrical fragment (P.N.127.7). They contain 1%, 1.3%, 3.2% and 19.9% of lead respectively. It should be noted that in the case of the small cylindrical fragment there is a possibility that the result does not represent the actual concentration of lead in the object. Lead is not soluble in molten copper and therefore, when present in significant amounts, it has the tendency to occur as a dispersion of fine particles on the surface of the object (Giumlia-Mair 1992; Ingo *et al*. 2006; Chiavari *et al*. 2010). Since this is a surface analysis, there is a possibility that in the areas analysed such globules of lead were present. Nevertheless, even if the level of lead is not exactly 19.9% it must still be very high. The cylindrical shape of this small piece combined with the high lead content leads us to suggest that this may be a fragment from a rod tripod stand. Published chemical analysis of such stands (MacNamara & Meeks 1987: 58–59; Papasavvas 2001: 43–45), as well as yet unpublished analyses which we have carried out, indicate that such high levels of lead are common in this category of bronze artefact. As noted above, the pendant in the shape of a pomegranate may also have been part of a stand.

Arsenic (As) is detected in the majority of the studied objects, ranging from 0.04 to 0.5%, and only 13 objects have no arsenic content (see **Figure AV.7**). The concentration level is very low, indicating that arsenic was not being added as a deliberate alloying element. Although its presence may be the result of smelting polymetallic copper ores (Swiny 1982: 71), the only areas in the island where ores with high enough concentrations of arsenic suitable for the production of arsenical copper occur are Laxia tou Mavrou and Pevkos, which are located in the Limassol Forest, southwest of the Troodos massif (Gass *et al*. 1994: 183–184). Much more likely is the possibility that these objects were partially made of metal deriving from the

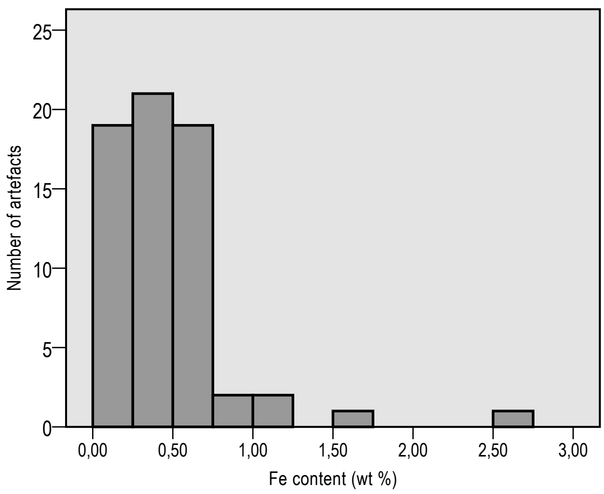

Figure AV.8. Histogram showing the concentration of iron (Fe) in the studied objects in weight %

recycling of objects dating to the Early and/or Middle Cypriote period which were made of arsenical copper. The fact that almost all objects that contain arsenic also contain tin confirms this possibility (Weinstein Balthazar 1990: 78). A good example is the broken dagger (P.N.128.4A), which has a tin content of 16.8% and an arsenic content of 0.3%. The arsenic indicates that the dagger was made of recycled metal and the fact that it was found broken in a hoard indicates that it was meant to be recycled again.

Iron (Fe) ranges from 0.08 to 1.5% with the exception of the pendant, which has an iron concentration of 2.5% (**Fig. AV.8**). In most of the cases concerning Cypriote artefacts made of copper alloys, where copper was produced mainly by the smelting of chalcopyrite (CuFeS2) (Constantinou 1982: 15; Tylecote 1982: 81), the presence of iron in various concentrations is not unexpected (Tylecote 1987: 300). Also, the use of iron oxides as a flux during the smelting procedure, in order to react and separate any associated silicon from the copper through the production of slag, might have resulted in the introduction of a small quantity of iron in the finished artefacts (Craddock & Meeks 1987: 192; Weinstein Balthazar 1990: 76; Ingo *et al*. 2006; Ashkenazi *et al*. 2012). Moreover, the presence of a small amount of the detected iron may be the result of soil contamination of the objects and of the diffusion of iron ions into the patina (Ingo *et al*. 2004: 202).

Zinc (Zn) is found only in 15 objects in the range 0.1 to 0.4%. Its presence can be justified as a non-intentional addition to the alloy, resulting from the smelting procedure, due to its occurrence in the copper sulphide ores (Constantinou 1982: 15).

AV.4 Conclusions

The chemical analysis of this assemblage of metal objects from the settlement of Pyla-*Kokkinokremos*, mainly composed of scrap metal, showed that the vast majority of them are bronzes. The fact that more than half of the assemblage has a tin concentration lower than 5% may indicate that tin was not available in abundance at this time. Indeed the only finds which had a tin content of over 9% were broken finished artefacts clearly ready to be recycled and perhaps could date to an earlier period. The low concentration of lead and the presence of arsenic in the majority of the objects with a significant amount of tin indicate that some of the objects under study were themselves made of recycled metal, some of which came from artefacts dating to the Early and Middle Bronze Age. Both the iron and the zinc are believed to be non-intentional additions to the alloys, resulting from the smelting procedure, coming either from the copper ores or from the flux.

Although the settlement was peacefully abandoned and, therefore, the inhabitants would have had the chance to collect their valuable belongings including the metal objects, the fact that among the finds there is only a handful of complete objects, while the majority falls into different categories of scrap metal, indicates that the inhabitants of Pyla-*Kokkinokremos* were very frugal with their metal. They collected even the smallest drop or casting spill to use it again.