Archaeometallurgic Investigations in Slovenia
A History of Research on Non-Ferrous Metals

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Izvleček

Prve posamične raziskave kemijske sestave arheoloških predmetov v Evropi segajo v 18. stoletje. Natančnejše meritve in množične analize pa je omogočil šele razvoj novih analitskih metod v prvi polovici 20. stoletja. Tedaj so se začele v številnih evropskih laboratorijih sistematične spektralne raziskave, predvsem prazgodovinskih izdelkov iz bakra in bakrovih zlitin.

V Sloveniji sta začela, na pobudo Oddelka za arheologijo Univerze v Ljubljani, leta 1988 s sistematičnimi spektralnimi analizami kovinskih predmetov iz pozne bronaste dobe Narodni muzej Slovenije in Kemijski inštitut v Ljubljani. Raziskave z metodo ICP-AES, razširjene s sodelovanjem metalurške stroke, so zajele tehnološke postopke pri pridobivanju in obdelavi bakra in bakrovih zlitin. Dosedanji rezultati so plodno dopolnili arheološko podobo in vlogo slovenskega prostora na prehodu 2. v 1. tisočletje pr. n. š.

Abstract

The first investigations of the chemical composition of archaeological artifacts in Europe were carried out in the 18th century. A decisive change occurred in the first half of the 20th century when the development of new analytical methods enabled measurement of very small quantities of material and a large number of analyses could thus be performed. This marked the start of systematically planned spectral analyses, particularly of prehistoric artifacts made of copper and copper alloys, at numerous European laboratories.

Systematic chemical research of Late Bronze Age metal objects in Slovenia began in 1988. This research was initiated by the Department of Archaeology (University of Ljubljana) and organised by the National Museum of Slovenia and the-National Institute of Chemistry in Ljubljana. The research, including also metallographic analyses, is directed towards a better understanding of the technology involved in the acquisiton and production of copper and copper alloys. The results of our investigation contribute to the archaeological understanding of the role played by the territory of Slovenia during the transitional period of the 11th/10th century BC.

A SUMMARY OF EUROPEAN STUDIES

Among humanistic sciences it is particularly the study of prehistoric ages that increasingly involves the natural sciences. The desire to completely understand the early development of human societies and their environments, together with the lack of written records, is leading archaeologists to broaden the scope of their investigations with a variety of natural scientific investigations from biological, anthropological and medicinal to geological, mineralogical, metallurgical and others. In addition to the standard archaeological methods of stratigraphy, typology and relative chronology, the use of chemical analyses and physical methods has increased. Due to their precise nature and rapid development of technical capabilities, archaeology is able to constructively fulfill its determinations. The use of physical methods is particularly successful in investigations concerning raw materials such as metal, stone, clay, amber and glass, where analyses of the chemical composition help in determining the origin, extraction, processing and distribution of material as well as finished products.

Chemists first took an interest in the composition of archaeological finds already towards the end of the 18th century as they began to examine Roman coins, glass and bronze objects. Chemical analyses of a larger amount of finds were first published in the 19th century, as well as articles in which natural scientists compare the composition of archaeological metals to their origins and chronological classifications (Caley 1967). A possible reason why these topics then failed to draw the attention of archaeologists was that analyses at that time did not yet generate results that were constructive enough to compensate for the damage done by taking samples from the finds. The chemical analytical method at that time required a considerable sample (1-2 g), while it only enabled the measurements of elements with high values and was not sufficient for successful research of metals (Pernicka 1998a). A decisive change occurred in the first half of the 20th century with the development of new analytical methods enabling the measurement of even very small amounts of material. In addition to the *chemical wet analysis* in use at the time, a new *instrumental* analysis method - *optic emission spectroscopy* (OES) - began to be applied in the beginning of the 1930's. Due to its properties - such as a more rapid course of analysis, the requirement of a smaller sample (50 mg and less), the capability of revealing elements in traces, a graphic analysis record in the form of a spectrum - this method was quickly recognized for analyzing archaeological finds. It was the first method which allowed a very large number of analyses to be carried out and thus stimulated the beginning of systematic investigations, especially of prehistoric metals (Winkler 1935; Pernicka 1990).

A history of the first spectral investigations has already been thoroughly discussed and evaluated (Härke 1978; Sangmeister 1998), and in particular from the point of view of applied analytic methods (Pernicka 1984; 1990); consequently, only a short review shall be contributed here. The greatest complex of methodically planned analyses was carried out during the period between the thirties and seventies of this century. Investigations unfolded within numerous collaborating laboratories in Europe. Copper and bronze finds from the Eneolithic and Early Bronze Age were the most frequent objects of analysis (approx. 60 000), followed by gold finds (approx. 4 500), and analyses of other metals (iron, antimony, tin and silver) and other materials, predominantly pottery. Glass, fine pottery, flint and obsidian, were also analyzed, although much fewer. All investigations shared the same basic purpose - to determine the composition of the products and the origin of the raw material.

The first period, during which the leading laboratories were located in Halle, Vienna, Stockholm and Leningrad /St. Peterburg/, was marked by the publication of analyses carried out in Halle (Otto, Witter 1952), including also the analysis of select prehistoric finds from Slovenia. During the next period, after 1946, when the network of collaborating laboratories expanded through all of Europe laboratories in Stuttgart, London, Oxford, Rennes, Lyon, Milan, Moscow, and elsewhere joined the investigations - Vienna and Stuttgart assumed the leading roles. The main aim of the Vienna team, under the leadership of R. Pittioni, was to determine the origins of ores, on the basis of which a relation between the ore deposit and the artifact could be established. This is why systematic field survey was performed in addition to spectral investigations of ores, although limited to the region of Austria (Pittioni 1957; 1959). Unfortunately, only semiquantitative results were applied during the analyses: the composition of elements was not recorded in percentages, but rather using symbols representing the presence, absence or trace of an element. This approach proved to be inappropriate as these results cannot be expressed quantitatively and therefore are not applicable for precise comparisons (Christoforidis et al. 1988; Pernicka 1990). On the contrary, the Stuttgart team, under the leadership of S. Junghans, decided to run a project within a European framework. More or less chronologically limited to the Copper and Early Bronze Ages this investigation incorporated spectral analyses of artifacts, as well as a comparison of their compositions. The analyses were grouped regarding the contents of five elements (arsenic, antimony, silver, nickel and bismuth). This provided the basis for regional groups of copper products to be determined as well as the local sources of raw material (Junghans et al. 1960; 1968; 1974). The Stuttgart laboratory completed its investigations in the 1970's, as did most other laboratories, with the exception of Moscow. Beginning in the 1960's, a group led by Černych has been carrying on systematic investigations concerning ore provenance (Černych 1992; 1998).

The superb work carried out by these laboratories, all using the same, excellent new analytical method, nevertheless failed to produce a final answer concerning the origin of the ore. Their results underwent critical evaluation and revision. The critical discussion concerning the interpretation of results from the Stuttgart laboratory was especially severe. It was demonstrated that the majority of established groups cannot be reliably allocated, either in time or space, and that the processing of results ensued from metallurgically oversimplified hypotheses on the copper ore sources, its processing and manufacture. In fact, the analyses failed to solve the main problem - the origin of the ore. Several critiques were also directed towards the reliability of the analyses carried out in Stuttgart (e.g. Boomert 1975; Coles 1982). Later examinations reinstated the analytic reliability of the Stuttgart investigations, once a large number of comparative analyses were carried out on individual elements using new methods (NAA and AAA) demonstrating the relatively small (30 %) deviation of the Stuttgart results. E. Pernicka, who took a detailed interest in reexamining the results, evaluated them to be a reliable bank of information well worth supplementing (Pernicka 1984; 1990). The famous group laboratory work was thus concluded. According to several estimations, the greatest number of analyses were carried out in Stuttgart, Vienna and Moscow - a total of at least 400 000 which is the number currently recorded in the Stuttgart database. The entire number could indeed add up to twice as much together with the unpublished analyses still preserved in the Moscow laboratory (Pernicka 1998a).

Investigations of metals persisted on into the third phase, which is considered effective from the late 1970's onwards and is still ongoing today (Pernicka 1998a). As already mentioned the results from the second phase of investigations were less than encouraging. To determine the relation between the product and the ore deposit proved to be much more arduous a task than initially anticipated. A study of trace elements in copper ore demonstrated that the variability of the elemental concentrations within the same ore deposit is rather large. It often coincides with the element pattern from another ore deposit. It seems that the main reason for differences in the ore composition is its position in the parent rock, which is related to the exposure to atmospheric conditions. It has been finally realized that all comparisons of trace element compositions in ores and artifacts are questionable. At the same time, the influence of metallurgic processes (melting, alloying, casting) performed on the metal on its way from the mining place to the smith's workshop proved to be highly significant regarding the elemental composition of an artifact (Craddock, Giumlia-Mair 1988).

It seems that the driving force of the third period of investigations remained the desire to determine the ore provenance despite the failure of previous efforts. New analytic methods, developed during the 1980's, greatly contributed to new attempts. Due to the low limits of detection, they are enabling the measurements of very small quantities of elements (traces). Those which are destructive require only several ten milligrams of a sample; if non-destructive, the investigated object needs to measure only a few centimeters. *Atomic absorption spectroscopy* (AAS), *neutron activation analysis* (NAA), *X-ray fluorescence* (XRF and PIXE) and *inductively coupled plasma - atomic emission spectroscopy* (ICP-AES) and *mass spectroscopy* (ICP-MS) are most frequently used to analyze copper alloys⁻. AAS and NAA are qualitative and quantitative methods, since they determine the type and amount of each element. However, the former method requires a long time and the latter method is very expensive (it requires an atomic reactor); consequently, these two methods are more appropriate for analyzing smaller numbers of objects and for testing results from other analyses. XRF and PIXE are semiquantitative methods, determining only the surface composition of an object. ICP-AES is a qualitative and quantitative method, it is precise regarding trace elements, as well as inexpensive in comparison with other methods. It enables a relatively simple and simultaneous determination of a very large number of elements (up to 70) from a very small sample. It also successfully overcomes the problem of nonhomogeneity. Despite the destruction of the sample (the recommended sample amount is cca 50 mg to enable result verification), this method was estimated as one of the most suitable methods for analyzing large numbers of archaeological metal objects (Pernicka 1984; 1990).

Lead isotope analysis has brought on a new zealousness for investigation of the ore provenance, in addition to *secondary ion mass spectroscopy* (SIMS), which was introduced recently for tracing selenium and tellurium in copper (Adriaens; Adams 1996; Adams et al. 1997). Lead isotope analysis is based on the ratio between three lead isotopes in copper which remains unchanged despite all physical and chemical processes through which a metal passes from the ore to the final product. A lead isotope ratio from an ore deposit can thus be obtained from a certain number of ore analyses which are then compared with the lead isotope ratio of the artifact. If the patterns do not match, it can be concluded that this ore deposit was not the source for the particular artifact. This analytical method was initiated in the investigations on the Late Bronze Age copper deposits and oxhide ingots in the eastern Mediterranean on Crete, Cyprus and Sardinia (Gale, Stos-Gale 1982).[1] It should be emphasized that, during the 1980's, the first investigations on

[1] Gale, Stos-Gale 1986a; 1986b; Gale 1989; Lo Schiavo et al. 1990.

ore deposits and metal finds dating to the Eneolithic and Early Bronze Age were established in the classic territories of the earliest metallurgy - in the Near East, Asia Minor and the eastern Mediterranean (Muhly 1985).[2] Among currently running investigations are German projects probably of the largest scale. Support from the Volkswagen fund promoted these investigations to strengthen the role of natural sciences in humanities, i.e. to support the development of *archaeometry*.[3] Between the years 1987 and 1997 the support was primarily intended for the development of *archaeometallurgy.* A series of large-scale projects were carried out during this period, which incorporated collaborating researchers from the Max-Planck Institute for Nuclear Physics in Heidelberg and for Chemistry in Mainz, the Würtemberg Regional Museum in Stuttgart, the Institute for Prehistory at the University in Heidelberg and the RGZM in Mainz, as well as others. The above mentioned areas in the Near East, Asia Minor, the Aegean and the eastern Mediterranean, as well as the Balkans - more precisely Serbia and Bulgaria, were included in the research plan with the intention to solve the problem of ore provenance.[4] The development of copper and bronze metallurgy during the Early Bronze Age in Europe, more precisely the region of the Unjetice culture (central and eastern Germany), has been investigated since 1990 (Krause 1998). Investigations of tin bronzes and tin deposits in Uzbekistan and Tajikistan have also been under investigation recently (Pernicka 1998c; Alimov et al. 1998).

Investigations of artefacts concerning the technological procedures of extracting, producing and alloying metals also augmented alongside investigations of ore deposits, with English researchers taking the lead. These investigations are evidently not run systematically, as are the German investigations, yet they are replete with brilliant ideas, observations and determinations from the field of metallurgy (Craddock 1978).[5] Early metallurgic skills are gradually being revealed through precise studies of the type and quantity of elements , as well as through the knowledge of the basic principles of metallurgic processes and various experimental efforts (Merkel 1990). A series of investigations was dedicated to Bronze Age metallurgy and trade in the eastern Mediterranean - Cyprus, Crete and Greece,[6] in the western Mediterranean - Sardinia[7] and Spain (Rothenberg and Blanco-Freijeiro 1981), and also the British Isles (Northover 1980; 1982b).

Analyses of objects dating to later periods and archaeometallurgic investigations of smaller areas in Europe are also increasing. Systematic investigations of copper, copper alloys and metallurgic activity during the Middle and Late Bronze Ages were carried out in Switzerland (Rychner 1990; Rychner, Kläntschi 1995), as well as analyses of Middle and Late Bronze Age hoard finds and analyses of La T ne bracelets in the Czech Republic (Frána et al. 1995 and 1997), metallographic investigations of bronze products in Italy (Antonacci Sanpaolo et al. 1992; Casagrande et al. 1993; Bietti Sestieri et al. 1998), analyses of products dating to the Early Bronze Age and hoard finds dating to the 10th century BC from Rio de Huelva in Spain (Roira 1995; Rovira and Gómez-Ramos 1998), and also individual smaller complexes of analyses and studies of bronze objects from the Iron Age, such as those in the region of Caput Adriae (Giumlia-Mair 1996; 1998) and Switzerland (Northover 1998).

INVESTIGATIONS IN SLOVENIA

Investigations of metals in Slovenia were quite modest up to the end of the 1980's compared with the analyses throughout Europe. Nevertheless, the first references of the chemical composition of metal finds are noted at the end of the 19th century and the beginning of the 20th century in publications of Müllner and Šmid (Müllner 1892; Šmid 1908). Slovenia was also included in the first spectral analyses of prehistoric copper and bronze finds carried out in laboratories in Halle and Stuttgart. Four pieces of raw material from the Črmošnjice Late Bronze Age hoard and one piece from the Jurka vas hoard, more than 40 primarily copper objects from the Ljubljana moor and other

[2] Muhly 1989; Muhly et al. 1991; Pernicka et al. 1984.

[3] Pernicka 1998b; Krause, Pernicka 1996. I would like to thank A. Preložnik for bringing these articles to my attention.

[4] Pernicka 1990 (1995), with rich references for all the mentioned areas.

[5] Oddy (ed.) 1991; Craddock (ed.) 1980; Craddock, Hughes (eds.) 1985; Craddock 1986; Tylecote 1992; Rothenberg 1991.

[6] *Early Metallurgy in Cyprus 5000-4000 BC*, Acta of the Int. Arch. Symp., Larnaca (Cyprus) (1981); Hallager 1985; Smith 1987.

[7] *Studies in Sardinian Archaeology* 3, BAR Int. Ser. 387 (1987); Lo Schiavo et al. 1990; Stos-Gale, Gale 1992.

smaller sites,[8] as well as the majority of prehistoric gold jewelry[9] have been analyzed. The reason for the deficiency of spectral analyses carried out by Slovene researchers was not so much due to Slovene archaeologists being uninformed, but rather primarily to a deficiency in funds necessary for these analyses. The considerable lack of interest of the majority of Slovene natural scientists to collaborate is also noticed. This situation might partly be explained by the extremely expensive nature of the majority of instruments for analytical methods (sometimes even an atomic reactor is required). Nevertheless, several analyses were indeed carried out due to friendly connections between the researchers on each side.

The first spectral analyses of eight prehistoric finds were initiated by S. Gabrovec in 1977. His friend and chemist, L. Kosta, together with colleagues, analyzed eight objects from the Udje hoard and from the Črmošnjice hoard (Kosta, Pihlar, Smodiš 1979). A combination of electrolysis, voltammetric methods and NAA was applied and ten elements were determined, also present in traces. The investigation was performed correctly, and also the interpretation of the results. According to current knowledge of characteristic element compositions of the Late Bronze Age metals, it can be said that the entire pattern of element compositions is in accordance with the average BA D-Ha A content of metals. The exception represents sample 7, which the authors also regarded as deviating from the other samples. The extremely high values of lead and zinc noted in this sample are highly unusual for this period and must be wrong unless the sample originated from another unknown archaeological site. These analyses proved that Slovene natural sciences could also apply the current instrumental methods (NAA) and the researchers were informed of the similar investigations throughout Europe. Unfortunately, the samples were published without inventory numbers, which renders a comparison of the results rather difficult. Their efforts also failed to motivate archaeologists to continue with further investigations in this topic.

The next analyses carried out in 1982 can also be assigned to the friendship of archaeologists and the natural scientist and physicist, Ž. Šmit. A. Pleterski and T. Knific selected two metal drops from a melting-pot and three samples of slag to be analyzed, as well as a group of seventeen various metal objects (mostly jewelry) from two archaeological sites, Pristava at Bled and Dlesc near Bodešče. Šmit applied a method of proton induced x-ray emission analysis (PIXE).[10] This method is nondestructive, however the analysis is limited to the thin surface layer of the object (up to a depth of 0.01-0.1 mm). It can serve only as a starting point for evaluating the composition of the whole object, with an approx. 10% accuracy. The researched objects were selected from three chronological periods (Roman, Early Middle Ages and Slavic) and from two sources (a settlement and a cemetery) with the intention of determining possible connections between the content of the melting-pot and the finished products (Šmit 1983). The analyses indicated that the composition of copper alloys corresponded to metallurgic principles, at least as far as the lead and tin content is concerned. It differed from the composition of drops in the melting-pot. However, the composition of the alloys did not seem characteristic for the individual chronological period. The slag proved to be iron and thus without any connection to the remaining objects. The selection of objects analyzed was of course too small and they were selected from too many various contexts to enable any sort of wider conclusions. This is what the author was also well aware of. It is not evident whether the author attempted to compare his analyses with current similar studies elsewhere in Europe.

The attempt of Ž. Šmit and P. Kos to solve numismatic problems with the same method followed. Sixteen small Norican silver coins from Celje and a part of the large Norican silver coins from the Bevke Celtic coin hoard were analyzed with the intention to determine the reason for variation in the weight ratio of the same type of small silver coins from two mints, at Magdalensberg (Kärnten, Austria) and at Celje (Slovenia). The coins from Celje are by a third lighter in weight than those from Magdalenska gora (Šmit, Kos 1984). As the surface analyses did not show any essential differences in the silver content, three small silver coins were cut in half to measure the concentration profiles. It was determined that the interior of the coins contains a much lesser quality silver than the surface. However, the results from the surface analyses could not serve for the determination of

8 See Otto, Witter 1952, 204, 206 for plano-convex ingots and see SAM 2/3 (1968) 10-13, 56-57, 142-143 and SAM 1 (1960) 119, 153 for copper products.

9 Concerning analyses of gold products check SAM 3 (1970) 65, 67- 68.

10 He thus enabled the possibility of nondestructive investigations of the object surface, e.g. tinning.

the average content of silver in the coins. This was probably the first, although modest, chemical study of an archaeological problem initiated by a numismatic. This investigation would still seem from today's point of view a test of the analytical capabilities of a method rather than an organized attempt, to solve a numismatic problem.

The First Systematic Investigations

In view of all the above mentioned, rather random analyses, the appeal to Slovene archaeologists by B. Teržan for methodical spectral analysis of ores, metals and products from throughout Slovenia, remained almost unnoticed (Teržan 1983; 1989). Teržan firmly established the need for chemical investigations of metal through her accurate studies on geological, mineralogical, vegetational and archaeological evidence of early mining on Pohorje. At the same time, she also pointed out the extensive foreign experiences with spectral analyses of copper and copper alloys, which seems highly appropriate considering the development of archaeometallurgic investigations in Europe, which were right at this time, during the 1980's, starting to flourish again. Following this appeal, an interdisciplinary project was announced in 1984/1985 at the Department of Archaeology, University of Ljubljana, under the title of "Archaeology of the Environment and Technologies". B. Slapšak clearly defined the aims of the natural science investigations in Slovene archaeology, especially those of metal, pottery and glass wares. He emphasized the fundamental significance of questions concerning the origins, processing and transport of raw material and finished products. Unfortunately, this project was never realized. Nevertheless, Teržan did not give in and the initiative for metal analysis did not wane. Following the first international colloquium on the Bronze Age in Slovenia, a new appeal to Slovene natural scientists was directed in 1987 at the Bronze Age exhibition at the National Museum in Ljubljana to turn their professional interests also towards the past. This time the effort proved worthy and perhaps the critique in the daily papers was also helpful.[11] The well considered selection of archaeological finds and the correct selection of analytical method proved to be decisive factors in initiating the first domestic systematic investigations. B. Teržan, as the initiator and the leader of investigations, selected hoard finds from the Late Bronze Age and B. Orel selected the analytic technique (ICP-AES). He also coordinated the financial support which could afford a larger number of analyses. The enormous number of analyses so easily recognized in investigations elsewhere in Europe seemed to be the condition *sine qua non* for attaining useful results. This could hardly be achieved only on the basis of friendly collaboration with researchers. The appropriate financial means for such analyses would have to be provided. The selection of finds was the result of numerous factors. Perhaps the primary factor was the greater amount of metal finds from the Late Bronze Age as compared to the earlier periods in Slovenia. The nature of these finds also seems important, as the vast majority are from hoards. These were considered very suitable for the initial analyses as their specific compositions promised interesting results. The majority of hoards contain relatively large groups of the same type of artifact, thus enabling reliable, statistically supported processing and a comparison of results within the individual groups, as well as between the various groups (*fig. 1*). Our aim was to attain a large enough number of systematically performed analyses which we could compare with the corresponding analyses elsewhere. As the ICP-AES method requires a sample, the selected objects were again, suitable for drilling, due to their size and solidity. It was easy to cover the traces of sampling (which was excellently executed by the National Museum Conservation Laboratory) and to preserve a large enough amount of the sample for eventual verification of the results.

The National Institute of Chemistry in Ljubljana hospitably "opened their doors" to us in 1988. The Laboratories of Analytical Chemistry (V. Hudnik) and Spectroscopy of Materials (B. Orel) decided to participate. The National Museum agreed to the one-year specialization of one of its staff (Z. Milić, a chemist) in ICP-AES techniques and the Research Council of Slovenia financially supported it. N. Trampuž Orel was allowed, at the same time, to dedicate a large part of her time to archaeometallurgic topics to be able to organize all further investigations. The entire project was also strongly supported by the Museum leadership.

[11] Popit I., Bronasti maček v žaklju, *Delo,* Friday, 22nd May 1987, 4. I would also like to mention the article by M. Budnar, Institute of Jožef Stefan, who a month later, also in the *Delo* newspaper, presented, as a natural scientist, the possibilities of the PIXE method for use in archaeology.

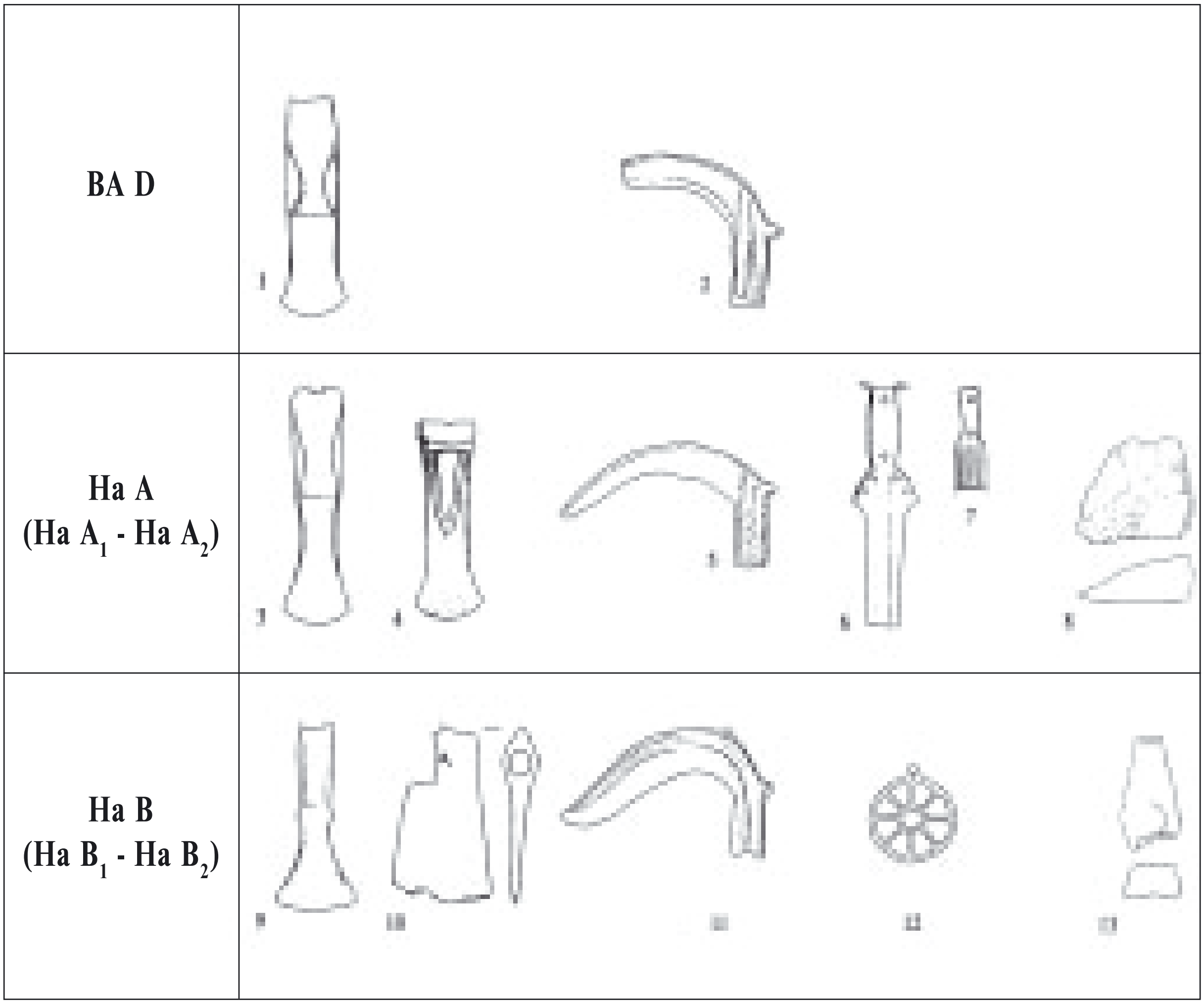

Fig. 1: Objects from Slovene hoards characteristic for the BA D, Ha A and Ha B periods (13th - 9th centuries BC).
Sl. 1: Izdelki iz slovenskih depojev, značilni za Bd D, Ha A in Ha B obdobje (13.-9. st. pr. n. š.).

The first analyses were carried out upon the material kept in the store-department of the National Museum of Slovenia - approximately one hundred analyses by the end of 1989. Our initial and unpretentious wish to determine the metal composition and structure was finally coming true. The first results were encouraging - copper-tin alloys were noticed in artifacts and pure copper in plano-convex ingots from the first two hoards. Variations in the tin content suggested a deliberate alloying. Moreover, lower amounts of tin noticed in sickles compared to the higher amounts of tin in axes, swords and spears suggested a production of deliberate copper-tin alloys for different purposes, i.e. for tools or weapons (Trampuž Orel et al. 1991). It was then decided that the investigation would be extended to all hoards from the southeastern Alpine region, dating to the Ha A and Ha B periods. The National Museum had to appeal to more than ten museums throughout Slovenia and in neighboring countries for samples. Our colleagues in Slovenia, Austria and Italy agreed to cooperate without delay and generously allowed for the sampling of objects and taking of photographs. I would like to acknowledge them again.

The Purpose of Investigations

The extent of our future work seemed large enough to demand a set of clearly defined aims of research. In contrast to most European archaeometallurgical investigations concerning the origins of ore, our studies, aided by the appropriate quantitative and qualitative analyses, were directed towards determining the technological processes involved in melting, alloying and casting metals. Researches carried out in our vicinity, in the Trident, the South and North Tirol and in the Eastern Alps, are primarily concerned with revealing traces of

Bronze Age mining and smelting of copper ores, as well as experimental work (Piel, Hauptmann, Schröder 1992; Čierny, Weisgerber, Perini 1992).[12] Investigations thematically similar to ours, concentrated on artifact production, have been underway since 1987 in Italy, although they contain either metallographic analyses (Casagrande et al. 1993; Antonacci Sanpaolo, Canziani Ricci, Follo 1992) or they are based upon the XRF method (Bietti Sestieri et al. 1998), whose imperfections in terms of systematic research have already been accounted for. The extensive investigations of copper and copper alloys in Switzerland represent thematically the closest research to ours, regarding the analytical method and the chronological period. The results enabled researchers to define the production areas for metal artifacts in the western Alps (Rychner 1981, Rychner; Kläntschi 1995). It was these results that we started to compare with our studies in the southeastern Alpine metallurgy (Trampuž Orel, Klemenc, Hudnik 1993).

Work Approach

Due to eventual verifications of our analyses, it was decided to publish the entire procedure, from the acquirement of samples, sample preparation and standard solutions, the selection of 12 elements to analyze (Sn, Pb, Fe, As, Sb, Ni, Co, Zn, Bi, Mn, Ag and Cu), the selection of spectral lines and detection limits to the problems concerning the representativity and homogeneity of the samples (Klemenc et al. 1992). Regarding the processing of results it was determined from the very start that the analyses within individual hoard finds will be joined into groups that represent objects of the same type - i.e. the analysis of sickles are followed by the analysis of axes, spears, etc. The total of the average values of all elements was added at the end of each group of analyses. We were especially careful with the chronological classification of the finds when comparing results. First a comparison of analyses within the same chronological level was carried out and the pattern attained was then compared with the new chronological level. As the analyzed finds originate from various parts of Slovenia, we were also cautious of any possible geographic variation. Therefore all results were initially processed inside each individual site. A better overview of the chemical and archaeological properties of the individual groups was thus attained. Comparisons within and between the groups were easier, and the exceptional chemical contents were more noticeable. This was a new way of presenting chemical analyses of archaeological objects that was not yet evidenced elsewhere among the published analyses of the time, at least not as consistently as it was presented in all our publications.[13]

Investigation Objectives

It soon became evident that the analyses would be capable of providing answers to much more demanding and complex questions than those initially anticipated. Our objectives were therefore set in accordance with the following questions which guided our investigations over the next ten years:

1. Are the differences in the alloy compositions dependent on: a) different degrees of development in prehistoric metallurgy; b) different chronological periods; c) different sources of raw materials; d) diverse purposes of the finished products?
2. Is it possible to determine the process of smelting and alloying metals by analyzing plano-convex ingots and cast ingots?
3. Is it possible to identify the traffic and trade network and the craft circle to which the southeastern Alpine region belonged at the end of the Late Bronze Age and the beginning of the Early Iron Age?

The analytical work was continued in 1990 by S. Klemenc, who did a larger number of analyses within the framework of her master's degree.[14] In her master's thesis,[15] she presented the already published application of the ICP-AES method for investigating archaeological finds (Klemenc et al. 1992), as well as the use of the chemometric methods - the Principal Component Analyses (PCA) and the method of hierarchical grouping - for processing a large amount of multidimensional data.[16]

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[12] Hauptmann, Marzatico, Perini 1993; Herdits 1993.

[13] Trampuž Orel et al. 1991, pl. 2 and 3 as well as all further publications of our analyses.

[14] S. Klemenc' master's degree was supervised by V. Hudnik within the project that was financed by the Research Council of Slovenia; Klemenc was temporarily employed at the National Museum of Slovenia.

[15] S. Klemenc, *Študij značilnosti arheoloških predmetov pozne bronaste dobe z ICP-AES in kemometrično analizo* (1993) master's thesis, University in Ljubljana, typescript.

[16] This is to the merit of J. Zupan, the researcher in the field of chemometrics at the National Institute of Chemistry in Ljubljana.

She also added a table of analyses which she had carried out (approximately 400 analyses for 11 hoard finds), while she concentrated on interpreting the compositions of plano-convex ingots rather than of artifacts (95 analyses for 7 hoard finds). It is quite satisfying that the archaeological initiative for analyses and the selected material served successfully as the subject matter of the master's degree in chemistry. After all, there are not many young chemists in Slovenia who would opt for research work in archaeology rather than in chemical industry.

Initial Results

At this stage of investigations we decided to include metallurgical investigations restricted to single objects and ingots.[17] The attempt of the metallurgic study on the extraction of copper, based on metallographic analyses of plano-convex ingots from Jurka vas, dates to this time (Paulin, Smolej 1993a; 1993 b). M. Doberšek was invited to examine our hypothesis on the production of sickles from deliberate copper alloys with low amounts of tin, which could sustain regular whetting and forging (N. Trampuž et al. 1991). His microstructural analyses of three sickles with low tin content confirmed our expectations - the sickle blade was forged. He also discovered that fresh copper was used for making bronze alloys for sickles, as opposed to the remelted scrap bronze. The discovery of deliberate copper alloys with low tin used for the production of sickles in the workshops of the Carpathian craft circle craft circle was a novelty, compared to other investigations elsewhere and especially in Western Europe, where larger amounts of tin were added to copper irrelevant of the type of artifact. Our metallurgical research also confirmed that at least select sickles found in hoards were used as harvest tools. This is in contradiction with the widely spread opinion that the primary role of those sickles was of a votive or pre-monetary nature. The discovery that fresh copper was used for casting sickles during the Late Bronze Age also speaks against the general conviction that only remelted scrap bronze was used for new products during the Late Bronze Age (Trampuž Orel et al. 1996).

The number of chemical analyses had increased in the meantime by the helpful work of V. Kos. Already 928 analyses were performed on finds from 23 hoards by 1995. The project became one of the few current, extensive investigations of Late Bronze Age artifacts in Central Europe. Such a large number of results presented an obstacle at the time. The importance of applying computer-statistical methods became inevitable. Furthermore, we also needed a new collaborator, a chemist, to continue with future analyses. However, young Slovene chemists were, quite understandably, faced with better perspectives in the pharmaceutical industry than in archaeometallurgy. At that moment, D. J. Heath, an environmental scientist, solved our problem when he came to Slovenia in 1995 and joined us. Despite his decision, which was primarily to "make a living", he was immediatelly enthusiastic about our investigations and deeply involved in archaeological problems, as no other researchers had been so far. Due to his computer processing of the results and his willingness to heed to the problems and needs in archaeology, the first six years of research were excellently concluded. The results were published, according to the plan made by B. Teržan, together with a presentation of all hoards and individual finds from the Bronze Age in Slovenia (Teržan 1996; Trampuž Orel, Heath, Hudnik 1996).

Conclusions

The results of this investigation show that the composition of copper alloys in our Late Bronze Age hoards depended on the technological knowledge of ancient smiths as well as upon the various sources of raw material. The period between the 12th and 11th centuries BC (the Ha A period) is characterized by various types of copper alloys with tin; the smiths carefully selected the alloy relevant to the type and purpose of the finished product. A resilient and malleable bronze, which was attained by adding a small enough amount of tin (approximately 4 %) to copper was most suitable for sickles. The sickle made of ductile bronze could sustain a frequent, alternate whetting and forging necessary for maintaining a sharp blade that would not break. Copper alloys with a larger amount of tin (6 %-9 %) were also produced, resulting in a hard bronze suitable for striking weapons (swords, spears) and tools (axes). This bronze sustained whetting, although the higher amounts of tin prevented it from requiring

[17] I would like to thank Mr. I. Kralj, an engineer of applied metallurgy, for all useful discussions and advices.

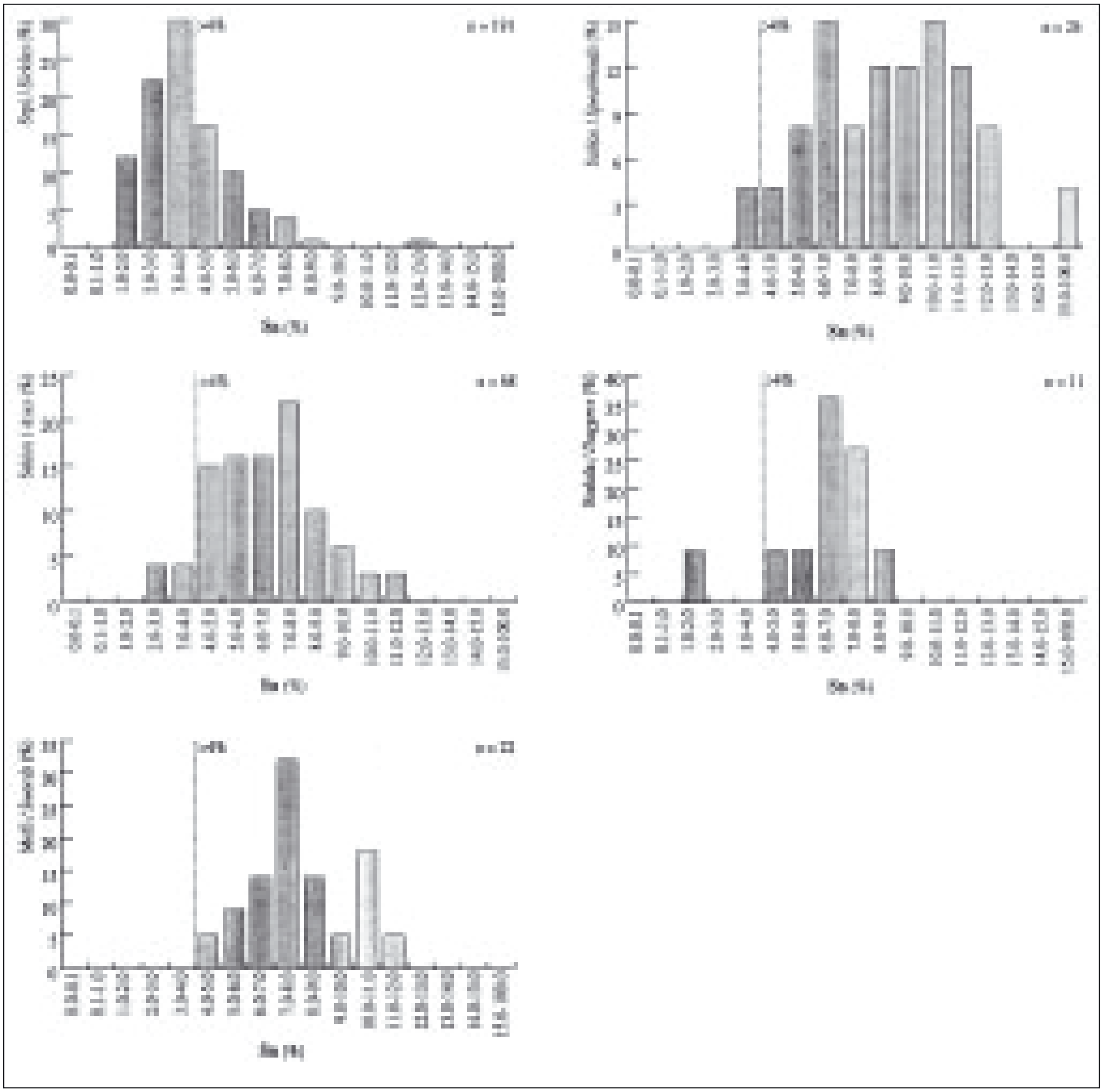

Fig. 2: Frequency histograms of varying compositions of tin in sickles, axes, spears, daggers and swords from hoards dating to the Ha A period in Slovenia (12th-11th centuries BC).
Sl. 2: Različna vsebnost kositra, prikazana s histogrami pogostnosti, v srpih, sekirah, sulicah, bodalih in mečih iz depojev Ha A obdobja v Sloveniji (12.-11. st. pr. n. š.)

hammering (*fig. 2*). This economical approach to tin was first discovered through our investigations. It was also statistically well supported and hypothetically linked with products of the Carpathian craft circle, due to the typological similarities of the Slovene artifacts (Trampuž Orel et al. 1991).[18] The link was also confirmed later by Liversage (1995). He arrived at similar conclusions through Stuttgart analyses of sickles, axes and swords from the Late Bronze Age hoards (of the IVth and Vth level after Moszolics) in Pannonia along the upper Tisa river. It should be stressed that smiths in western parts of Europe failed to display such metallurgical expertise with tin alloys (Craddock

[18] Trampuž Orel, Klemenc, Hudnik 1993; Trampuž Orel, Heath, Hudnik 1996. The same craft-circle was recently determined by typological classification of sickles from Slovenia (P. Pavlin, Bronzezeitliche Griffzungensicheln mit Y-Motiv, *Arh. vest.* 48, 1997, 27-40.

Fig. 3: Slovenia in relation to the Carpathian craft circle during the Ha A period (12th-11th centuries BC), as indicated by the results from spectral analyses.
Sl. 3: Razmerje Slovenije do karpatskega prostora v Ha A obdobju (12.-11. st. pr. n. š.), kot ga kažejo rezultati spektralnih analiz.

1978; Rychner 1995). This additionally increases the significance of metallurgy in the Carpathian region. This data adds to our understanding of the close links between the social communities in the area extending from the Friuli region at the west to the southeastern Transdanubian region at the east and the Austrian Styria to the north (Turk 1996). Additionally, we may assume that during the last two centuries in the 2nd millennium BC, the population of the Slovene region was incorporated in the economic and perhaps also political sphere of the Carpathian region (*fig. 3*).

Research revealed a noticeable change in the technology and use of raw materials during the transition to the 1st millennium (Ha A2/Ha B1). In contrast with the earlier periods, when leaded copper or bronze alloys were practically absent among the analyzed objects, except the rare examples, the use of lead as an additive to the alloy is evidenced as characteristic for the 1st millennium BC. Lead is not represented as a pure metal but always as a binary alloy with copper or as a ternary alloy with copper and tin, in objects and ingots, often in surprisingly high amounts. It is quite evident that smiths already knew the role played by lead in obtaining a higher quality in cast objects. That this technology was also in use in the region of Slovenia is confirmed by numerous finds of fragments of shaft-hole axes, primarily from hillforts in Inner Carniola, almost all of which are made of copper alloys with high amounts of lead. The fragments are supposed to be used by a local smith to improve the quality of casting (Trampuž Orel, Heath 1998).

A new type of a raw material is also available in abundance - ingots, (cast in molds). Contrary

Fig. 4: Slovenia in relation to the Apennine peninsula at the beginning of the Ha B period (11/10th-9th centuries BC), as indicated by the results from spectral analyses.
Sl. 4: Razmerje Slovenije do Apeninskega polotoka v začetku Ha B obdobja (11./10.-9.st. pr. n. š.), kot ga kažejo rezultati spektralnih analiz.

to the simple plano-convex ingots, the cast ingots, just by their shape, indicate the new type of metal to be processed. The copper used for products during this period is quite different to that used during the previous period, as it contains high amounts of impurities, primarily antimony, and can thus be attributed to sulphide ores of the Fahlerz type. Again, our research was faced with the need for collaboration with geologists (U. Herlec) and metallurgists (A. Paulin). Their studies were concentrated on the new types of metals. According to the composition of some of our ingots, classified as "speiss" (D. Heath), it was supposed that not only deposits rich with tetrahedrite were worked during this period, but also deposits with more complex ores containing, also other minerals rich with cobalt and nickel (Paulin et al. 1999). Archaeologically insufficiently researched deposits of these types are also located in our vicinity in various parts of the Alps and in central Italy. The distribution of artifacts most similar to those found in Slovenia, especially those containing considerable amounts of lead, ranging from wheel-shaped pendants to shaft-hole axes and ingots, is primarily in the regions west of Slovenia (central and northern Italy, Switzerland). On the one hand, this suggests that the use of leaded copper alloys spread from the Apennine peninsula toward the regions on the north and east, including Slovenia (*fig. 4*); while on the other hand, this distribution is revealing an almost diametric contradictory situation where the region of Slovenia found itself in the 1st millennium BC in comparison to the earlier periods. Trade and social contacts, influenced by the technological novelties linked the region of Slovenia primarily with the northern Adriatic, Friuli and the Paduan lowlands and possibly also central Italy on the one hand and the Alpine valleys in the north and west on the other. New deposits, including those with complex ores and metal trade evidently represented important reasons for new "western" contacts, and probably also new trade routes. The valley of the Soča river and its tributaries, as well as the Idrija and Cerklje regions started to play an important role. The research conclusions are in the perfect agreement with the wider view of cultural and economic connections, as considered by Teržan, between the eastern Mediterranean and the Alps (which incorporated also the western Balkans and the Italian peninsula) during the 11th/10th centuries BC. The new situation is directly related to the prospecting new ore deposits and the spread of the new technologies of copper as well as iron (Teržan 1995; 1996).

The research results (some have attracted the attention of the wider European region) were stimulative enough to advocate the continuation of our work (Hänsel 1998; Jockenhövel 1998; Frána et al. 1997). We would like to confirm our current results on finds from neighboring regions and compare them with the chemical pattern of different chronological periods. We are particularly interested in the metal technologies at the end of the Late Bronze Age and at the beginning of the Iron Age, as it could prove to be essential for our understanding of the origins of ironworks in the Slovene region.

Recent investigations, mostly from the past two years,[19] of individual metal objects or objects linked with the processing of metal during prehistoric, as well as other periods, should not be overlooked. The same is true for archaeometric investigations of other types of materials and chronological periods, including amber and resin,[20] pottery, glass[21] and stone tools,[22] as well as dendrochronological and magnetometric investigations.[23]

The Purpose of Archaeometallurgic Investigations

A review of investigations in Slovenia demonstrated that a larger part of metal research (as well as other materials) was directed toward individual objects and answering questions, usually referring to the unknown composition of a metal or other material. These otherwise successful investigations contributed satisfying answers to some extent. They also proved to be obligatory for completing the "identification card" for each find and for good quality conservatory treatment of the object. However, they failed to contribute

[19] Select investigations were the result of the conservation work, such as Z. Milić, J. Rant, I. Nemec, Uporaba nevtronske radiografije pri konserviranju rimskega bodala, *Argo* 40/1, 1997, 135-141; J. Rant et al., *Proc. of the 4th Int. Conf. on NDT of Works of Art* (Berlin 1994) 31-40 and J. Rant et al., *Proc. of the 5th World Conf.* (Berlin 1997) 742-749. Others are the result of archaeological excavations and an interest in metallurgy: Velušček, Greif 1998 as well as Šmit, Nečemer 1998; or directly connected with investigations of the Late Bronze Age hoards in Slovenia (D. J. Heath, N. Trampuž Orel, Visual properties of prehistoric alloys: analyses of copper based artefacts by ICP-AES, in: *11th Int. Conf. Spectroscopy in Theory and Practice, Bled, 11.-15. 4. 1999*, *Book of Abstracts*, 89. These investigations also stimulated collaborating metallurgists to independent studies on the material: Paulin, Herdits 1996; Paulin et al. 1998; M. Doberšek, A. Paulin, *Kovine, zlitine, tehnologije* 32, 1998, 99-103; Paulin 1998; 1999 - these studies still require comments of an archaeologist! Investigations on metal finds dating to the Early Middle Ages are also running (a cooperation between the National Museum of Slovenia and the Institute Jožef Stefan in Ljubljana).

[20] Hadži, Cvek 1976; J. Puš, Premazi in smolnati kit na prazgodovinskih posodah, *Arh. vest.* 27, 1976, 124-127; Hadži, Orel 1978; concerning the methods and results of these investigations see also Trampuž Orel 1990.

[21] M. Daszkiewicz, G. Schneider, Chemical, Mineralogical and Technological Studies of Fabrics of Roman Vessels and Lamps from Poetovio, in: J. Istenič, *Poetovio - zahodna grobišča*, Kat. in monogr. (1999) (in preparation for print); I. Klopčič, Mineralogical Research on the Neolithic Ceramic Assemblage from Moverna vas, in: *Recent Developments in Yougoslav Archaeology*, BAR Int. Ser. 431 (1988) 201-209; M. Novič, M. Novič, J. Zupan, B. Križ, Chemometric Evaluation of the ICP-AES Analyses of Archaeological Samples, in: *11th Int. Conf. Spectroscopy in Theory and Practice, Bled, 11.-15. 4. 1999, Book of Abstracts,* 147; the referred investigation possibly relates to the chemical study on archaeological finds from Novo mesto, e.g. M. Novič, *Vzorčevanje in elektrokemijska analiza arheoloških zlitin iz obdobja žarnih grobišč* (1979) (graduate thesis, FNT Ljubljana) as well as Ž. Šmit, P. Pelicon, G. Vidmar, B. Zorko, M. Budnar, P. Kump, M. Nečemer, Analysis of Medieval Glass by Proton Induced X-ray Emmission Spectroscopy, in: *11th Int. Conf. Spectroscopy in Theory and Practice, Bled, 11.-15. 4. 1999, Book of Abstracts,* 107.

[22] S. Petru, Metode preiskav sledov uporabe na kamenih orodjih iz najdišč Zakajeni spodmol in Mala Triglavca. *Por. razisk. pal. neol. eneol. Slov.* 24, 1997, 79-97; Ž. Šmit, S. Petru, G. Grime, M. Budnar, T. Vidmar, B. Zorko, M. Ravnikar, Usewear-Induced Deposition on Prehistoric Flint Tools, in: *Nuclear Instruments and Methods in Physics Research* B 140 (1998) 209-216.

[23] B. Mušič, L. Orengo, Magnetometrične raziskave železnodobnega talilnega kompleksa na Cvingerju pri Meniški vasi, *Arh. vest.* 49, 1998, 157-186; K. Čufar, T. Levanič, A. Velušček, Dendrokronološke raziskave na koliščih Spodnje mostišče 1 in 2 ter Hočevarica, *Arh. vest.* 49, 1998, 75-92.

towards a better understanding of the role of the Slovene region during the archaeological periods in general, and the prehistoric period in particular. They did, however, contributed to the comprehension that systematic investigations are a necessity in order to reach this aim; the scientific potential and the perfectly technically equipped natural science institutes in Slovenia enable this. Despite such high quality support from the natural science, it would be, of course, futile to expect successful results from a research in the absence of a well considered archaeological plan. The problems concerning archaeometallurgy are integral and they usually exceed the boundaries of smaller regions. Collaborating natural scientists, who have yet to be trained in archaeometallurgy, therefore need a full assistance and relevant informations from responsible archaeologists. Clearly defined archaeological topics, incorporating the entire region, as well as accurately considered and extensive selection of finds, originating from firmly classified contexts, are needed for a well planned project. The optimal analytical method and a suitably selected interdisciplinary research team, in which archaeologists need to contribute equivalently and actively collaborate with natural scientists in the processing and interpretation of results, are also necessary. The Ministry for Science and Technology in Slovenia casually supported these types of research in the past, for which we are grateful. Since 1998 a regular support to natural scientific researches in the humanities started; it is hoped that this will contribute in systematic archaeometric investigations, including archaeometallurgic ones. The recently established Field Research Center, led by the main archaeological institutions (Institute of Archaeology of the Scientific Research Centre of the Slovene Academy of Sciences and Arts, the Department of Archaeology on the University of Ljubljana, and the National Museum of Slovenia) is a step in the right direction.

ADAMS, F., A. ADRIAENS, A. AERTS, I. DE RAEDT, K. JANSSENS and O. SCHALM 1997, Micro and Surface Analysis in Art and Archaeology. - *Journal of Analytical Atomic Spectrometry* 12, 257-265.

ADRIAENS, A. and F. ADAMS 1996, The Application of Ion Microprobe Analyses and Other Beam Methods in Archaeological Research. - In: Aggarwal, S. K. and H. C. Jain (eds.), *Seventh National Symposium on Mass Spectrometry*, Nov. 26-28, 1996, 4-14, Gwallior.

ALIMOV, K., N. BOROFFKA, M. BUBNOVA, J. BURJAKOV, J. CIERNY, J. JAKUBOV, J. LUTZ, H. PARZINGER, E. PERNICKA, V. RADILILOVSKIJ, V. RUZANOV, T. ŠIRINOV, D. STARŠININ and G. WEISGERBER 1998, Prähistorischer Zinnbergbau in Mittelasien. - *Eurasia Antiqua* 4, 137-199.

ANTONACCI SANPAOLO, E., C. CANZIANI RICCI and L. FOLLO 1992, Il deposito di San Francesco (Bologna) ed il contributo delle indagini archeometallurgiche. - In: *Archeometallurgia. Ricerche e prospettive.* Atti del colloquio intern. di archeometallurgia (Bologna 1988) 159-206, Bologna.

BIETTI SESTIERI, A. M., C. CANEVA, C. GIARDINO, G. E. GIGANTE, R. MAZZEO, C. MORIGI GOVI, A. PALMIERI and S. RIDOLFI 1998, Production and functions of Early Iron Age metal artefacts from the Bologna area: archaeometallurgical research on the bronze hoard from San Francesco (Bologna). - In: *Proceedings of the XIII Congress* (Forl 1996) Vol. 4, 801-808, Forli.

BOOMERT, A. 1975, A contribution to the classification of spectro-analyses of prehistoric metal objects. - *Helinium* 15, 134-161.

CALEY, E. R. 1967, The early history of chemistry in the service of archaeology. - *Jour. Chem. Education* 44, 120-128.

CASAGRANDE, A., G. L. GARAGNANI, E. LANDI, E. PELLEGRINI and P. SPINEDI 1993, Indagini analitico-strutturali su reperti metallici di etŕ Protostorica dell'Italia continentale: Dati e considerazioni preliminari su un programma di ricerca pilota. - *St. Etr.* 58, 255-272.

CHRISTOFORIDIS, A., E. PERNICKA and H. SCHICKLER 1988, Ostalpine Kupferlagerstätten und ihre Bedeutung für die prähistorische Metallgewinnung in Mitteleuropa. - *Jb. Röm. Germ. Zentmus.* 35, 533-536.

COLES, J. M., 1982, The Bronze Age in northwestern Europe: problems and advances. - In: Wendorf, F. and A. E. Close (eds.), *Advances in World Archaeology* 1, 265-321, New York.

CRADDOCK, P. T. 1978, Deliberate Alloying in the Atlantic Bronze Age. - In: Ryan, M. (ed.), *The Origins of Metallurgy in Atlantic Europe*. Proc. of the fifth Atlantic Colloquium, 369-385, Dublin.

CRADDOCK, P. T. (ed.)1980, Scientific Studies in Early Mining and Extractive Metallurgy. - *British Museum Occasional Paper* 20.

CRADDOCK, P. T. 1986, The Metallurgy and Composition of Etruscan Bronze. - *St. Etr.* 52, 211-271.

CRADDOCK, P. T. 1995, *Early metal mining and production.* - Edinburgh.

CRADDOCK, P. T. and A. R. GIUMLIA-MAIR 1988, Problems and possibilities for provenancing bronzes by chemical composition. - In: *Bronzeworking centres of western Asia c. 1000-539 BC,* 317-326, London, New York.

CRADDOCK, P. T. and M. J. HUGHES (eds.) 1985, *Furnaces and Smelting Technology in Antiquity.* - British Museum Occasional Paper 48.

ČERNYCH, N. E. 1992, *Ancient metallurgy in the USSR.* - Cambridge.

ČERNYCH, N. E. 1998, Ancient mining and metallurgy in Eastern Europe: ecological problems. - In: Hänsel, B. (ed.), *Mensch und Umwelt in der Bronzezeit Europas,* 129-133, Kiel.

ČIERNY, J., G. WEISGERBER and R. PERINI 1992, Ein spätbronzezeitliche Hüttenplatz in Bedollo/Trentino. - In: Lippert, A. and K. Spindler (eds.), *Festschrift zum 50jährigen Bestehen des Institutes für Ur- und Frühgeschichte der Leopold-Franzens-Universität Innsbruck,* Universitätsforschungen zur prähistorischen Archäologie 8, 97-105.

FRÁNA, J., L. JIRÁN, A. MAŠTALKA and V. MOUCHA 1995, Artifacts of copper and copper alloys in prehistoric Bohemia from the viewpoint of analyses of element composition I. - In: *Praehistorica Archaeologica Bohemica 1995,* Pam. arch. Suppl. 3, 127-296.

FRÁNA, J., L. JIRÁN, V. MOUCHA and P. SANKOT 1997, Artifacts of copper and copper alloys in prehistoric Bohemia from the viewpoint of analyses of element composition II. - In: *Praehistorica Archaeologica Bohemica 1997,* Pam. arch. Suppl. 8.

GALE, N. H. 1989, Archaeometallurgical studies of Late Bronze Age oxhide copper ingots from the Mediterranean region. - In: Hauptmann, A., E. Pernicka and G. A. Wagner (eds.), *Old World Archaeometallurgy,* Der Anschnitt. Beiheft 7, 247-268, Bochum.

GALE, N. H and Z. A. STOS-GALE 1982, Bronze Age Copper Sources in the Mediterranean: A New Approach. - *Science* 216, 11-19.

GALE, N. H and Z. A. STOS-GALE 1986a, Anatolian and Cycladic Metal Sources. - *PACT* 15, 13-30.

GALE, N. H and Z. A. STOS-GALE 1986b, Oxhide ingots in Crete and Cyprus and the Bronze Age metals trade. - *Ann. Brit. Sch. Ath.* 81, 81-100.

GIUMLIA-MAIR, A. 1995, The copper-based finds from a Slovenian Iron Age site. - *Bulletin of the Metals Museum* 23, 59-81, Sendai, Japan.

GIUMLIA-MAIR, A. 1998, Studi tecnici sui bronzi dell'officina dei Castiei. - In: Cassola Guida, P., S. Pettarin, G. Petrucci and A. Giumlia-Mair (eds.), *Pozzuolo del Friuli - II, 2.* - Studi e ricerche di protostoria mediterranea 5, 183-233, Roma.

HADŽI, D. and F. CVEK 1976, Smolni kit in premaz za žare. - *Arh. vest.* 27, 128-134.

HADŽI, D. and B. OREL 1978, Spektrometrične raziskave izvora jantarja in smol iz prazgodovinskih najdišč na Slovenskem. - *Vest. slov. kem. dr.* 25/1, 51-62.

HALLAGER, B. P. 1985, Crete and Italy in the Late Bronze Age III Period. - *Amer. Jour. Arch.* 89, 293-305.

HÄNSEL, B., Die Bronzezeit als erste europäische Epoche. - In: Hänsel, B. (ed.), *Mensch und Umwelt in der Bronzezeit Europas,* 19-26, Kiel.

HÄRKE, H. 1978, Probleme der optischen Emmissionsspektralanalyse in der Urgeschichtsforschung. - *Praehist. Ztschr.* 53, 165-276.

HARTMANN, A. 1970, *Praehistorische Goldfunde aus Europa.* - SAM 3.

HAUPTMANN, A., F. MARZATICO and R. PERINI 1993, Ricerca archeometallurgica - Importanti studi in Val dei Mocheni e Luserna. - *Identita - Notiziario trimestrale dell'Istituto Culturale Mocheno Cimbro* 10, marzo 1993, 2-9.

HERDITS, H. 1993, Zum Beginn experimentalarchäologischer Untersuchungen einer bronzezeitlichen Kupferverhüttungsanlage in Mühlbach, Salzburg. - *Arch. Austr.* 77, 31-38.

JOCKENHÖVEL, A. 1998, Mensch und Umwelt in der Bronzezeit Europas: Einführung in die Thematik. - In: Hänsel, B. (ed.), *Mensch und Umwelt in der Bronzezeit Europas,* 27-47, Kiel.

JUNGHANS, S., E. SANGMEISTER and M. SCHRÖDER 1960, *Metallanalysen kupferzeitlichen und frühbronzezeitlicher Bodenfunde aus Europa.* - SAM 1, Berlin.

JUNGHANS, S., E. SANGMEISTER and M. SCHRÖDER 1968 and 1974, *Kupfer und Bronze in der frühen Metallzeit Europas.* - SAM 2/1-3 and SAM 2/4, Berlin.

KLEMENC, S., B. BUDIČ, V. HUDNIK and Z. MILIĆ 1992, The application of ICP atomic emmission spectrometry to the analysis of metal artifacts from Late Bronze Age. - *Vest. slov. kem. dr.* 39/4, 461-469.

KOSTA, L., B. PIHLAR and B. SMODIŠ 1979, Trace elements as indicators of the origin of ancient alloys from Slovene finds. - *Vest. slov. kem. dr.* 26/3, 249-259.

KRAUSE, R. and E. PERNICKA 1996, Das neue Stuttgarter Metallanalysenprojekt "SMAP". - *Archäol. Nachrbl.* 1/3, 274-291.

LIVERSAGE, D. 1994, Interpreting composition's patterns in ancient bronze - the Carpathian Basin. - *Acta Arch.* 65, 57-134.

LO SCHIAVO, F., R. MADDIN, J. MERKEL, J. D. MUHLY and T. STECH 1990, *Metallographic and statistical analyses of copper ingots from Sardinia.* - Quaderni 17, Ozieri.

MERKEL, J. 1990, Experimental reconstruction of Bronze Age copper smelting based on archaeological evidence from Timna. - In: Rothenberg, B. (ed.), *The ancient metallurgy of copper.* - London.

MUHLY, J. D. 1985, Sources of Tin and the Beginnings of Bronze Metallurgy. - *Amer. Jour. Arch.* 89/2, 275-291.

MUHLY, J. D. 1989, Çayönü Tepesi and the beginnings of metallurgy in the Ancient World. - In: Hauptmann, A., E. Pernicka and A. G. Wagner (eds.), *Old World Archaeometallurgy,* Der Anschnitt. Beiheft 7, 1-11.

MUHLY, J. D., F. BEGEMANN, Ö. ÖZTUNALI, E. PERNICKA, S. SCHMITT-STRECKER and G. A. WAGNER 1991, The bronze metallurgy of Anatolia and the question of local tin sources. - In: Pernicka E. and G. A. Wagner (eds.), *Archaeometry '90,* 209-220, Basel.

MÜLLNER, A. 1892, *Argo* 1/5, 99.

NORTHOVER, P. 1980, The analysis of Welsh Bronze age metalwork. - In: Savory, N. H., *Guide catalogue of the Bronze age collections,* 229-243, Cardiff.

NORTHOVER, P. 1982a, The metallurgy of the Willburton hoards. - *Oxford Journal Arch.* 1, 69-109.

NORTHOVER, P. 1982b, The Exploration of the Long-distance Movement of Bronze in Bronze and Early Iron Age Europe. - *Bull. Inst. Arch.* 19, 45-72.

NORTHOVER, P. 1998, Analysis of copper alloy metalwork. - In: Schindler, M., *Der Depotfund von Arbedo TI und die Bronzedepotfunde des Alpenvorraumes vom 6. Bis zum Beginn des 4. Jh.v.Chr.,* Annex 1, 289-316, Basel.

ODDY, W. A. (ed.) 1991, *Aspects of Early Metallurgy.* - Brit. Mus. Occasional Paper 17.

OTTO, H. and W. WITTER 1952, *Handbuch der altesten vorgeschichtlichen Metallurgie in Mitteleuropa.* - Leipzig.

PAULIN, A. 1998, Speiss- term and origin of word. - *Materiali in geookolje* 45/3-4, 437-477.

PAULIN, A. 1999, Early making metals. - *Rudarsko-metalurški zbornik* 46/1, 59-81.

PAULIN, A. and A. SMOLEJ 1993a, O tehnologiji pridobivanja bakra v Evropi v bronasti dobi (1st and 2nd part). - *Rudarsko-metalurški zbornik* 40/1-2, 203-219 in 221-232.

PAULIN, A. and A. SMOLEJ 1993b, Technology of copper smelting in the Late Bronze Age. - *Minerals Industry International* 1012, 16-20.

PAULIN, A. and H. HERDITS 1996, An idea how ancient copper smelters could have discovered smelting of metallic iron. - *Rudarsko-metalurški zbornik* 43/1-2, 125-135.

PAULIN, A., M. JERAM, S. SPAIĆ and L. KOSEC 1998, Studies on Copper-Iron Alloys. - *Metall* 52/7-8, 438-442.

PAULIN, A., S. SPAIĆ, S. SPRUK, D. J. HEATH and N. TRAMPUŽ OREL 1999, Speiss from the Late Bronze Age. - *Erzmetall* 52/11 (in print).

PERNICKA, E. 1984, Instrumentelle Multi-Elementanalyse archäologischer Kupfer- und Bronzeartefakte: ein Methodenvergleich. - *Jb. Röm. Germ. Zentmus.* 31, 517-531.

PERNICKA, E. 1987, Erzlagerstätten in der Ägäis und ihre Ausbeutung im Altertum: geochemische Untersuchungen zur Herkunftbestimmung archäologischer Metallobjekte. - *Jb. Röm. Germ. Zentmus.* 34/2, 607-714.

PERNICKA, E. 1989, Zur Probenahme von archäologischen Metallobjekten. - *Arbeitsblätter* 1/19, *Naturwissensch. Untersuchungen*, 138-148.

PERNICKA, E. 1990, Gewinnung und Verbreitung der Metalle in prähistorischer Zeit. - *Jb. Röm. Germ. Zentmus.* 37, 21-129.

PERNICKA, E. 1998a, Whither metal analysis in archaeology? - In: Mordant, C., M. Pernot and V. Rychner (eds.), *L'Atelier du bronzier, Bronze '96: colloque international, Neuchâtel et Dijon, 1996,* 259-267, Paris.

PERNICKA, E. 1998b, Förderschwerpunkt Archäometallurgie - Eine Bilanz. - *Archäol. Nachrbl.* 3/1, 79-85.

PERNICKA, E. 1998c, Die Ausbreitung der Zinnbronze im 3. Jahrtausend. - In: Hänsel, B. (ed.), *Mensch und Umwelt in der Bronzezeit Europas,* 135-147, Kiel.

PERNICKA, E., T. C. SEELIGER, G. B. WAGNER, F. BEGEMANN, S. SCHMITT-STRECKER, C. EIBNER, Ö. ÖZTUNALY and I. BARANYI 1984, Archäometallurgische Untersuchungen in Nordwestanatolien. - *Jb. Röm. Germ. Zentmus*. 31, 533-599.

PIEL, M., A. HAUPTMANN and B. SCHRÖDER 1992, Naturwissenschaftliche Untersuchungen an bronzezeitlichen Kupferverhüttungsschlacken von Acqua Fredda / Trentino. - In: Lippert, A. and K. Spindler (eds.), *Festschrift zum 50jährigen Bestehen des Institutes für Ur- und Frühgeschichte der Leopold-Franzens-Universität Innsbruck,* Universitätsforschungen zur prähistorischen Archäologie 8, 463-772.

PITTIONI, R. 1957, *Urzeitlicher Bergbau auf Kupfererz und Spurenanalyse. Beiträge zum Problem der Relation Lagerstätte-Fertigobjekt*. - Arch. Austr. Beih. 1.

PITTIONI, R. 1959, Zweck und Ziel spektralanalytischer Untersuchungen für die Urgeschichte des Kupferbergwesens. - *Arch. Austr*. 26, 67-95.

ROTHENBERG, B. (ed.) 1991, *The Ancient Metallurgy of Copper. Researches in the Arabah,* Vol. 2. - London.

ROTHENBERG, B. and A. BLANCO-FREIJEIRO 1981, *Studies in Ancient Mining and Metallurgy in South-west Spain*.

ROVIRA, S. 1995, Estudio arqueometalúrgico del depósito de la Ria de Huelva. - In: M., Ruiz-Gálvez (ed.), *Ritos de paso y puntos de paso: la Ria de Huelva en el mundo del Bronce final europeo,* 33-57, Madrid.

ROVIRA, S. and P. GÓMEZ-RAMOS 1998, The Ria de Huelva Hoard and the Late Bronze Age metalwork: a statistical approach. - In: Mordant, C., M. Pernot and V. Rychner (eds.), *L'atelier du bronzier en Europe, Bronze '96: colloque international, Neuchâtel et Dijon, 1996,* 81-90, Paris.

RYCHNER, V. 1981, Le cuivre et les alliages du Bronze final en Suisse occidentale: premieres analyses spectrographiques a Auvernier/Nord et a Neuchâtel/Le Cret. - *Musée neuchâteloise* 18, 97-124.

RYCHNER, V. 1990, L'analyse chimique du bronze préhistorique: pourquoi? - *Ztschr. Schweiz. Arch. u. Kunstg.* 47, 201-212.

RYCHNER, V. and N. KLÄNTSCHI 1995, *Arsenic, nickel et antimoine. Une approche de la metallurgie du Bronze moyen et final en Suisse par l'analyse spectrometrique* 1, 2. - Cahiers d'archéologie romande 63.

SAM 1, 1960 - see Junghans, Sangmeister, Schröder 1960.

SAM 2/3, 1968 - see Junghans, Sangmeister, Schröder 1968.

SAM 3, 1970 - see Hartmann 1970.

SANGMEISTER, E. 1998, Metallanalysen der Archäologie: Erfahrungen aus 45 Jahren Forschung. - In: Mordant, C., M. Pernot and V. Rychner (eds.), *L'Atelier du bronzier. Bronze '96: colloque international, Neuchâtel et Dijon, 1996,* 9-18, Paris.

SMITH, T. R. 1987, *Mycenean Trade and Interaction in the West Central Mediterranean 1600-1000 BC.* - BAR Int. Ser. 371.

STOS-GALE, Z. and N. H. GALE 1992, New light on the provenience of the copper oxhide ingots found on Sardinia. - In: Tykot, R. H. and T. K. Andrews (eds.), *Sardinia in the Mediterranean: A footprint in the sea,* Monographs in Mediterranean Archaeology 3, 317-346.

ŠMID, W. 1908, Altslovenische Gräber Krains. - *Carniola* 1, 17-44.

ŠMIT, Ž. 1983, Analiza kovinskih predmetov s protonsko vzbujenimi rentgenskimi žarki. - *Arh. vest.* 33, 191-196.

ŠMIT, Ž. and P. KOS 1984, Elemental Analysis of Celtic Coins. - *Nuclear Instruments and Methods in Physics Research* B 3, 416-418.

ŠMIT, Ž. and M. NEČEMER 1998, Sledovi metalurške dejavnosti na keramičnih fragmentih. - *Arh. vest.* 49, 55-61.

TERŽAN, B. 1983, Das Pohorje - ein vorgeschichtliches Erzrevier? - *Arh. vest.* 34, 51-84.

TERŽAN, B. 1989, Pohorje - prazgodovinski rudarski revir? - *Čas. zgod. narod.* 60/2, 238-260.

TERŽAN, B. 1995, Stand und Aufgaben der Forschungen zur Urnenfelderzeit in Jugoslawien. - In: *Beiträge zur Urnenfelderzeit nördlich und südlich der Alpen. Festschr. H. Müller-Karpe,* Monogr. Rom. Germ. Zentmus. 35, 323-372.

TERŽAN, B. 1996, Sklepna beseda (Conclusion). - In: Teržan, B. (ed.), *Depojske in posamezne kovinske najdbe bakrene in bronaste dobe na Slovenskem* 2, Kat. in monogr. 30, 243-258.

TRAMPUŽ OREL, N. and D. J. HEATH 1998, Analysis of Heavily Leaded Shaft-Hole Axes. - In: Hänsel, B. (ed.), *Mensch und Umwelt in der Bronzezeit Europas,* 237-248, Kiel.

TRAMPUŽ OREL, N., D. J. HEATH and V. HUDNIK 1996, Spektrometrične raziskave depojskih najdb pozne bronaste dobe (Spectrometric Research of the Late Bronze Age Hoard Finds). - In: Teržan, B. (ed.), *Depojske in posamezne najdbe bakrene in bronaste dobe na Slovenskem* 2, Kat.in monogr. 30, 165-242.

TRAMPUŽ OREL, N., S. KLEMENC and V. HUDNIK 1993, Spektrometrične raziskave poznobronastodobnih depojskih najdb Pušenci, Cerovec in Hudinja. - In: *Ptujski arheološki zbornik,* 159-170, Ptuj.

TRAMPUŽ OREL, N., M. DOBERŠEK, D. J. HEATH and V. HUDNIK 1996, Untersuchungen an Sicheln aus spätbronzezeitlichen Hortfunden Sloweniens. - *Praehist. Ztschr.* 71/2, 176-193.

TRAMPUŽ OREL, N., Z. MILIĆ, V. HUDNIK and B. OREL 1991, Inductively coupled plasma - atomic emission spectroscopy analysis of metals from Late Bronze Age hoards in Slovenia. - *Archaeometry* 32/2, 267-277.

TURK, P. 1996, Datacija poznobronastodobnih depojev (The Dating of Late Bronze Age Hoards). - In: Teržan, B. (ed.), *Depojske in posamezne kovinske najdbe bakrene in bronaste dobe na Slovenskem* 2, Kat. in monogr. 30, 89-124.

TYLECOTE, R. F. 1992, *A History of Metallurgy.* - London, Brookfield.

VELUŠČEK, A. and T. GREIF 1998, Talilnik in livarski kalup z Maharskega prekopa na Ljubljanskem barju. - *Arh. vest.* 49, 31-53.

WINKLER, J. E. R. 1935, *Quantitative spektralanalytische Untersuchungen an Kupferlegierungen zur Analyse vorgeschichtlicher Bronzen*. - Veröffentlichungen der Landesanstalt für Volkheitskunde zu Halle 7.

Arheometalurške raziskave v Sloveniji
Zgodovina raziskav prazgodovinskih barvnih kovin

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Med humanističnimi vedami prav prazgodovinska arheologija vedno tesneje sodeluje z naravoslovnimi vedami. Želja po celovitem razumevanju najstarejšega razvoja človeške družbe in njenega okolja in obenem soočanje s pomanjkanjem oziroma redkostjo pisnih virov, vodita prazgodovinske arheologe vse bolj v dopolnjevanje raziskav s paleto naravoslovnih raz-iskav od bioloških, antropoloških in medicinskih do geoloških, mineraloških, metalurških in drugih. Klasičnim arheološkim metodam stratigrafije, tipologije in relativne kronologije se pridružuje tudi uporaba kemijskih in fizikalnih metod, ki zaradi eksaktne narave in hitro razvijajočih se tehničnih zmogljivosti arheologiji omogočajo, da svoja dognanja plodno dopolnjuje z naravoslovnimi ugotovitvami. Uporaba fizikalnih metod je še posebej uspešna pri raziskavah osnovnih surovin, kot so kovina, kamen, glina, jantar in steklo, kjer analize kemijske sestave pomagajo pri reševanju vprašanj o izvoru, pridobivanju, predelavi in razširjanju surovine kot tudi izdelkov.

Zdi se, da je sestava arheoloških predmetov najprej začela zanimati kemike, ki so že proti koncu 18. st. pregledovali antične novce, steklene izdelke, pa tudi bronaste predmete. Iz 19. st. izvirajo prve objavljene kemijske analize večjega števila predmetov in članki, v katerih naravoslovci poskušajo primerjati sestavo arheoloških kovin z njihovim izvorom in časovno opredelitvijo (Caley 1967). Za arheologe ta tematika ni bila zanimiva, morda tudi zato, ker tedanje analize še niso dajale rezultatov, ki bi bili dovolj uporabni, glede na škodo, ki so jo povzročali odvzemi vzorcev na gradivu. Tedanja kemijska analitska metoda je namreč zahtevala kar precejšen vzorec (1-2 g), omogočala pa je le meritve elementov z visokimi vsebnostmi, kar ni bilo dovolj za uspešno raziskovanje kovin (Pernicka 1998a). Šele v prvi polovici 20. st. je nastopila odločilna sprememba, ko je razvoj novih analitskih metod omogočil meritve zelo majhnih količin snovi. Poleg do tedaj uporabljane *kemijske mokre analize*, se je v začetku 1930-ih let začela uveljavljati nova *instrumentalna* analitska metoda - *optična emisijska spektroskopija* (OES). Zaradi svojih lastnosti, kot je hitrejši potek analize, manjši vzorec (50 mg in manj), možnost odkrivanja elementov v sledovih, grafični zapis analize v obliki spektra, se je ta zelo hitro uveljavila za raziskovanje arheoloških predmetov in tako prvič omogočila res veliko število analiz in s tem začetek sistematičnih raziskav, predvsem prazgodovinskih kovin (Winkler 1935; Pernicka 1990).

Zgodovina prvih spektralnih raziskav je bila že izčrpno obdelana in ovrednotena (Härke 1978; Sangmeister 1998), še posebej tudi z vidika uporabljenih analiznih metod (Pernicka 1984; 1990), zato bo na tem mestu podan le kratek povzetek. Največji sklop načrtno zastavljenih analiz je bil opravljen v obdobju med 30. in 70. leti tega stoletja, ko so se raziskave odvijale v več med seboj povezanih evropskih laboratorijih. Najpogosteje so bili analizirani bakreni in bronasti predmeti iz obeh istoimenskih obdobij (približno 60 000), sledile so jim analize zlatih predmetov (4 500), manj številne pa so bile analize drugih kovin (železa, antimona, kositra in srebra) in drugih materialov, od katerih je bila povečini analizirana keramika, pa tudi steklo, fajansa, kremen ter obsidijan. Vse raz-iskave je družil osnovni namen - ugotoviti sestavo izdelkov in izvor surovine.

Prvo obdobje, v katerem so bili vodilni laboratoriji v Halleju, na Dunaju, v Stockholmu in tedanjem Leningradu, je zaznamovala objava analiz iz Halleja (Otto, Witter 1952), med katerimi so, naj omenim, tudi analize nekaterih slovenskih prazgodovinskih predmetov. V naslednjem, drugem obdobju, ko so je po letu 1946 mreža sodelujočih laboratorijev razširila po vsej Evropi - raziskavam so se pridružili še laboratoriji v Stuttgartu, Londonu, Oxfordu, Rennesu, Lyonu, Milanu, Moskvi in drugod - sta vodilno vlogo prevzela Dunaj in Stuttgart. Glavni namen dunajske ekipe pod vodstvom R. Pittionija je bila določitev rudnih izvorov, na osnovi katerih so hoteli dokazati povezavo med rudiščem in izdelkom, zato so poleg spektralnih raziskav rude sistematično pregledovali tudi teren, pri čemer so se omejili na območje Avstrije (Pittioni 1957; 1959). Pri analizah so žal uporabljali semikvantitativne rezultate - vsebnosti elementov niso izrazili v procentih, temveč le v simbolih za navzočnost, odsotnost ali sled. Izkazalo se je, da to ni bil pravi pristop in da njihovi rezultati niso uporabni za natančne primerjave, ker se jih ne da izraziti količinsko (Christoforidis, Pernicka, Schickler 1988; Pernicka 1990). Nasprotno se je stut-tgartska ekipa pod vodstvom S. Junghansa odločila za projekt v evropskem okviru, ki je bil kronološko bolj ali manj omejen na bakreno in zgodnjo bronasto dobo, in je vseboval spektralne analize predmetov in primerjavo njihovih sestavov. Analize so združevali glede na vsebnosti petih elementov (arzena, antimona, srebra, niklja in bizmuta) v skupine, na podlagi katerih so poskušali določiti regionalne skupine bakrenih izdelkov in s tem posredno tudi lokalne vire surovin (Junghans, Sangmeister, Schröder 1960; 1968; 1974). Stuttgartski laboratorij je prenehal z delom v 1970-ih letih, prav tako tudi večina ostalih skupin. Pač pa je načrtne analize, povezane z izvorom rude od 1960-ih let dalje izvajala v Moskvi skupina pod vodstvom Černycha (Černych 1992; 1998).

Veliko delo, ki so ga opravili omenjeni laboratoriji z odlično novo in enako metodo, vendar ni dalo dokončnega odgovora o izvoru rude. Rezultati so doživeli kritične ocene in revizije, posebno pri stuttgartskem projektu je bila kritika ostra do interpretacije rezultatov. Pokazalo se je, da večine ustvarjenih skupin ni mogoče zanesljivo razporediti niti v času niti v prostoru, in da je obdelava rezultatov izhajala iz metalurško preveč poenostavljene domneve o viru surovine, o njeni obdelavi in predelavi, in da analize pravzaprav ne morejo rešiti glavnega problema - izvora rude; nekatere kritike so bile namenjene tudi zanesljivosti stuttgartskih analiz (npr. Boomert 1975; Coles 1982). S poznejšimi preverjanji je bila analitska zanesljivost stuttgartskih raziskav rehabilitirana, potem ko je bilo opravljenih precejšnje število primerjalnih analiz posameznih elementov z novimi metodami (NAA in AAA), ki so pokazale razmeroma majhno (30 %) odstopanje stuttgartskih rezultatov. S preverjanjem rezultatov se je veliko ukvarjal E. Pernicka, ki jih je ovrednotil kot zanesljivo banko podatkov, vredno dopolnjevanja (Pernicka 1984; 1990). Znamenito skupinsko laboratorijsko delo je torej prenehalo; po nekaterih ocenah je bilo največje število analiz opravljenih v Stuttgartu, na Dunaju in v Moskvi - skupaj najmanj 400 000 - toliko jih namreč zdaj hranijo v stuttgartski podatkovni bazi. Celotno število, skupaj z neobjav-ljenimi analizami, ki jih še vedno hranijo v Moskvi, utegne biti še enkrat večje (Pernicka 1998a).

Raziskave kovin so se prevesile v tretje obdobje, ki ga štejejo od poznih 1970-ih dalje in traja še zdaj (Pernicka 1998a). Kot je bilo že omenjeno, rezultati drugega obdobja raziskav niso bili preveč opogumljajoči. Izkazalo se je, da je povezava med predmetom in rudnim virom veliko težje dokazljiva, kot pa je bilo to videti na začetku. Študij slednih elementov v bakrovi rudi je pokazal, da je spremenljivost vzorca slednih elementov znotraj istega rudišča dokaj široka in da se pogosto celo prekriva z vzorcem iz drugega rudišča. Videti je, da je glavni razlog tej različni sestavi rude njen položaj v kamnini in s tem v zvezi izpostavljenost vremenskim vplivom. Ob tem spoznanju so postale vse primerjave vsebnosti elementov v rudi z izdelkom vprašljive. Hkrati pa se je izkazalo, da je treba pri obravnavi sestave izdelka upoštevati vpliv metalurških postopkov (taljenja, legiranja, vlivanja), ki so bili opravljeni (ali: skozi katere gre) na kovini na poti od rudnika do končnega izdelka v livarjevih rokah (Craddock, Giumlia-Mair 1988).

Lahko bi rekli, da je kljub neuspehu v dotedanjih raziskavah še vedno ostala gonilna sila tretjega obdobja raziskav barv-nih kovin želja, da bi odkrili rudni izvor. K temu so veliko pripomogle nove analitske metode, ki so se razvile v 1980-ih letih in s katerimi je mogoče meriti zelo majhne količine snovi (sledne elemente), oziroma imajo zelo nizke meje zaznavnosti. So porušne, vendar zahtevajo le miligramske količine vzorca, ali pa so neporušne, vendar mora biti preiskovani predmet velik nekaj centimetrov. Za analiziranje bakrovih zlitin (torej izdelkov) se največ uporabljajo *atomska absorbcijska spektroskopija* (AAS), *nevtronska aktivacijska analiza* (NAA), *fluorescenca rentgenskih žarkov* (XRF in PIXE) ter *atomska emisijska spektroskopija z induktivno sklopljeno plasmo* (ICP-AES) in *masna spektroskopija* (ICP-MS). AAS in NAA sta kvalitativni in kvantitativni metodi, torej razkrijeta vrsto in količino posameznega elementa, vendar prva zahteva precej časa, druga pa je zelo draga (potreben je reaktor), zato sta bolj primerni za analiziranje majhnega števila predmetov in za preverjanje rezultatov drugih analiz. XRF in PIXE sta semikvantitativni metodi, poleg tega pa pokažeta le površinsko sestavo predmeta. ICP-AES je kvalitativna in kvantitativna metoda, natančna v območju sled-nih elementov in tudi cenena v primerjavi z drugimi metodami. Omogoča namreč razmeroma enostavno, sočasno določanje zelo velikega števila elementov (do 70) iz zelo majhne količine vzorca; uspešno pa tudi premaguje problem nehomogenosti . Kljub temu, da je porušna (zaradi možnosti preverjanja rezultatov je priporočena količina vzorca ca 50 mg), je bila ocenjena kot ena najprimernejših metod za analiziranje velikega števila arheoloških kovinskih predmetov (Pernicka 1984; 1990).

Raziskovanju rudnega izvora je poleg *masne spektroskopije* (SIMS, t. j. secondary ion mass spectrometry), s katero zasledujejo elementno razmerje selena in telurija v bakru in se uporablja v zadnjem času (Adriaens, Adams 1996; Adams et al. 1997), je pravi polet dala *analiza svinčevih* izotopov. Temelji na dejstvu, da ostaja razmerje med tremi svinčevimi izotopi v bakru nespremenjeno kljub vsakršnim fizikalnim in kemijskim postopkom, skozi katere gre kovina od rude do izdelka. Tako lahko dobimo izotopski vzorec nekega rudišča, ko opravimo določeno število analiz svinčevih izotopov, ki ga nato primerjamo z razmerjem svinčevih izotopov v izdelku. Če se vzorca ne ujemata, lahko sklepamo, da to rudišče ni bilo vir rude za omenjeni predmet. Z omenjeno metodo so začeli raziskovati bakrove vire in ox-hide ingote pozne bronaste dobe v vzhodnem Sredozemlju na Kreti, Cipru in Sardiniji (Gale, Stos-Gale 1982).[1] Nasploh so bile v 1980-ih letih zastavljene raziskave rudišč in kovinskih izdelkov iz eneolitika in zgodnje bronaste dobe na klasičnih ozemljih najstarejše metalurgije na Bližnjem Vzhodu, v Mali Aziji in vzhodnem Sredozemlju (Muhly 1985).[2] Trenutno pa so najbrž najbolj velikopotezne nemške arheometalurške raziskave, ki so bile načrtno zasnovane in so centralno vodene, omogočila pa jih je podpora Volkswagnovega sklada z namenom, da bi se okrepila vloga naravoslovja v kulturnozgodovinskih vedah - torej razvoj *arheometrije.*[3] Med leti 1987 in 1997 je bila podpora namenjena predvsem razvoju *arheometalurgije* in v tem obdobju je stekla cela vrsta velikih projektov, pri katerih sodelujejo predvsem raziskovalci Inštituta Max-Planck za jedrsko fiziko v Heidelbergu oziroma za kemijo v Mainzu, Würtemberškega deželnega muzeja v Stuttgartu, Inštituta za pred- in prazgodovino univerze v Heidelbergu in RGZM v Mainzu in drugi. V okviru tega načrta so preiskali že omenjena območja Prednje Azije, Bližnjega Vzhoda, Egeje oziroma vzhodnega Sredozemlja ter Balkana - natančneje Srbije in Bolgarije, vse z namenom, da bi našli dokončni odgovor na vprašanje o izvoru rud.[4] Od leta 1990 raz-iskujejo tudi razvoj metalurgije bakra in brona v zgodnji bronasti dobi v Evropi, natančneje na ozemlju unjetiške kulture in njenih vplivov, torej v osrednji in vzhodni Nemčiji (Krause 1998). V zadnjem času so se lotili tudi raziskav kositrovih bronov in ležišč kositra v Uzbekistanu in Tadžikistanu (Pernicka 1998c; Alimov et al. 1998).

Ob raziskavah rude so se množile tudi raziskave sestave izdelkov z vidika tehnoloških postopkov pridobivanja in predelave kovine in izdelave zlitin, v katerih zavzemajo vodilno mesto angleški raziskovalci. Te raziskave se očitno ne izvajajo v okviru nekega obširnega sistematičnega načrta, kot je primer nemških raziskav, vendar so polne blestečih idej, spoznanj in ugotovitev z metalurškega področja (Craddock 1978).[5] Z natančnim ugotavljanjem vrste in količine elementov v preiskovanem izdelku, s poznavanjem osnovnih zakonitosti metalurških postopkov in z eksperimentalnim delom postopoma razkriva-jo nekdanje metalurško znanje (Merkel 1990). Vrsta raziskav je bila posvečena bronastodobni metalurgiji in z njo povezani trgovini v vzhodnem Sredozemlju - na Cipru, Kreti ter v Grčiji[6] in v zahodnem Sredozemlju - na Sardiniji[7] in v Španiji (Rothenberg, Blanco-Freijeiro 1981) ter na Britanskem otočju (Northover 1980; 1982b).

Množijo pa se tudi analize izdelkov iz mlajših obdobij in arheometalurške raziskave manjših območij v Evropi, kot n. pr. sistematične raziskave bakra, bakrovih zlitin in metalurškega udejstvovanja v srednji in pozni bronasti dobi v Švici (Rychner 1990; Rychner, Kläntschi 1995), analize srednje-in poznobronastobnih depojskih izdelkov in analize latenskih zapestnic s Češkega (Frána et al. 1995 in 1997), predvsem metalografske raziskave bronastih izdelkov v Italiji (Antonacci Sanpaolo, Canziani Ricci, Follo 1992; Casagrande et al. 1993; Bietti Sestieri et al. 1998), analize izdelkov iz zgodnje bronaste dobe in depojske najdbe iz 10. st.pr. n. š. Ria de Huelva v Španiji (Rovira 1995; Rovira, Gómez-Ramos 1998) ter posamezni manjši sklopi analiz in študij bronastih premetov iz železne dobe, kot na primer z območja Caput Adriae (Giumlia-Mair 1996; 1998) in Švice (Northover 1998).

DOMAČE RAZISKAVE

V primerjavi s stanjem analiz v Evropi so bile raziskave vseh kovin v Sloveniji do konca 1980-ih let skromne. Vendar tudi pri nas zasledimo prve posamične omembe kemijske sestave kovinskih predmetov ob koncu 19. in na začetku 20. stoletja v Müllnerjevih in Šmidovih objavah (Müllner 1892; Šmid 1908). Prvih spektralnih analiz prazgodovinskih predmetov iz bakra in brona pa smo bili tudi mi deležni iz omenjenih projektov

[1] Gale, Stos-Gale 1986a; 1986b; Gale 1989; Lo Schiavo et al. 1990.

[2] Muhly 1989; Muhly et al. 1991; Pernicka et al. 1984.

[3] Pernicka 1998b; Krause, Pernicka 1996. Za posredovanje teh člankov se zahvaljujem A. Preložniku.

[4] Pernicka 1990, z izčrpno literaturo za vsa omenjena področja.

[5] Oddy (ed.) 1991; Craddock (ed.) 1980; Craddock, Hughes (eds.) 1985; Craddock 1986; Tylecote 1992; Rothenberg 1991.

[6] *Early Metallurgy in Cyprus 5000-4000 BC,* Acta of the Int. Arch. Symp.,Larnaca (Cyprus) (1981); Hallager 1985; Smith 1987.

[7] *Studies in Sardinian Archaeology* 3, BAR Int. Ser. 387 (1987); Lo Schiavo et al. 1990; Stos-Gale, Gale 1992.

nemških laboratorijev v Halleju in Stuttgartu - analizirani so bili štirje surovci iz poznobronastodobnega depoja Črmošnjice in en surovec iz sočasnega depoja Jurka vas ter več kot 40 povečini bakrenih predmetov z Ljubljanskega barja in iz drugih manjših najdišč[8] ter večina našega zlatega prazgodovinskega nakita.[9] Vzrok takemu stanju ni bila neobveščenost slovenskih arheologov, pač pa verjetno v prvi vrsti pomanjkanje denarja, ki bi bil potreben v ta namen, in verjetno s tem povezana nezainteresiranost večine slovenskih naravoslovnih raziskovalcev za sodelovanje. Aparature za instrumentalne metode so izredno drage, za nekatere je potreben celo reaktor, zato so tudi analize relativno drage. Kljub temu je bilo nekaj analiz opravljenih, kar gre pripisati predvsem prijateljskim stikom med raziskovalci na obeh straneh in čisto osebnemu zanimanju red-kih naravoslovcev za tako sodelovanje.

Tako smo leta 1977 dobili na pobudo S. Gabrovca prve domače spektralne analize osmih prazgodovinskih predmetov; njegov prijatelj kemik L. Kosta je skupaj s sodelavci analiziral osem predmetov iz tedaj odkritega depoja Udje in iz depoja Črmošnjice (Kosta, Pihlar, Smodiš 1979). Uporabili so kombinacijo elektrolize, voltametričnih metod in NAA in določili deset elementov, prisotnih tudi v sledovih. Raziskava je bila korektno izvedena, prav tako tudi interpretacija rezultatov. Z današnjim poznavanjem značilnih elementnih sestavov poznobronastodobnih kovin je mogoče reči, da celotna podoba elementnih vsebnosti ustreza povprečnemu sestavu Bd D-Ha A izdelkov, razen vzorca 7, za katerega so tudi avtorji menili, da odstopa od ostalih. Izredno visoki vrednosti svinca in cinka v omenjenem vzorcu, kakršnih navadno ni v omenjenem obdobju, sta napačni, če verjamemo podatku, da izvira vzorec iz enega od obeh omenje-nih depojev, ali pa je vzorec pripadal predmetu iz drugega, nenavedenega najdišča. Analize so dokaz, da je naše naravoslovje tudi tedaj uporabljajo najsodobnejše instrumentalne meto-de (NAA), da so bili omenjeni raziskovalci seznanjeni z najmanj eno od tedanjih podobnih vodilnih raziskav in tekočo problematiko (nehomogenost ipd.). Žal so vzorce predmetov objavili brez inventarnih številk, zato so rezultati težko primerljivi; predvsem pa njihovo delo ni vzpodbudilo arheologov k nadaljevanju raziskav na tem področju.

Tudi za naslednje analize iz leta 1982 je bilo zaslužno prijateljevanje arheologov z naravoslovcem fizikom Ž. Šmitom, ki se je iz lastne pobude začel ukvarjati z raziskovanjem sestave arheoloških kovinskih predmetov. A. Pleterski in T. Knific sta mu izbrala za analiziranje dve kovinski kaplji iz talilnega lončka in tri vzorce žlindre, dodali pa so še skupino sedemnajstih različnih kovinskih predmetov (večinoma nakit) s Pristave na Bledu in z Dlesc pri Bodeščah. Šmit je uporabil metodo v okviru svojih obstoječih eksperimentalnih možnosti, to je metoda protonsko vzbujenih rentgenskih žarkov (PIXE).[10] Omenjena metoda je nedestruktivna, vendar analiza zajame le plitvo površino predmeta do globine 0,01-0,1 mm, kar pomeni, da je analiza le izhodišče za oceno sestava celotnega predmeta in to s približno 10 % mersko natančnostjo. Preiskovani predmeti so bili izbrani iz treh časovnih obdobij (antičnega, zgodnjesrednjeveškega in slovanskega) in iz dveh virov (naselbine in grobišča) z namenom, da bi ugotovili morebitno zvezo med vsebino talilnega lončka in izdelki (Šmit 1983). Analize so pokazale, da se sestava bakrovih zlitin v predmetih ravna po metalurških pravilih, vsaj kar zadeva vsebnosti svinca in kositra, in da se razlikuje od sestave kapelj v lončku; pač pa se sestava zlitin ni zdela značilna za posamezno od časovnih obdobij. Žlindra se je izkazala za železovo in tako nima povezave z ostalimi predmeti. Seveda je bilo analiziranih predmetov premalo, izbrani pa so bili iz preveč različnih kontekstov, da bi raziskava omogočila kakršnekoli širše ugotovitve, česar se je zavedal tudi avtor. Iz njegove objave tudi ni razvidno, da bi domače analize poskušal primerjati z rezultati že znanih prej omenjenih tujih raziskav.

Sledil je še poskus Ž. Šmita in P. Kosa, da bi z isto metodo rešila numizmatično problematiko. Analiziranih je bilo 16 ma-lih noriških srebrnikov iz Celja in del velikih noriških srebrnikov iz depojske novčne najdbe iz Bevk z namenom, da bi na osnovi kemijske sestave ugotovili vzroke razlik v težnem razmerju istovrstnih malih srebrnikov iz dveh kovnic, Štalenske gore (Magdalensberg) na Koroškem in Celja; celjski novci so namreč za tretjino lažji od magdalenskogorskih (Šmit, Kos 1984). Površinske analize niso pokazale bistvenih razlik v vsebno-sti srebra, zato so tri male srebrnike razpolovili in izmerili koncentracijske profile. Izkazalo se je, da je notranjost novcev iz precej slabšega srebra kot površina, tako da iz rezultatov povr-šinskih analiz ni bilo mogoče sklepati na povprečno sestavo novcev. S to ugotovitvijo se je omenjena raziskava zaključila. Bila je - čeprav zelo skromna - verjetno prva, v kateri je arheolog dal pobudo za reševanje kompleksne strokovne problematike s kemijsko analizo kovine. Vendar se zdi, gledano z današnjega zornega kota, kot da je tudi ta raziskava bila bolj preizkus zmožnosti konkretne metode v arheoloških raziskavah, kot pa načrten poskus reševanja numizmatične neznanke.

Prve sistematične raziskave

Ob vseh naštetih posameznih, povečini naključnih analizah, je ostal poziv k načrtnim spektralnim analizam rude, kovine in izdelkov iz ožjega in širšega območja Slovenije, ki ga je B. Teržanova tedaj naslovila na slovenske arheologe, skorajda neopazen (Teržan 1983 in 1989). Ob studioznem prikazu geo-loških, mineraloških, vegetacijskih in arheoloških dokazov za začetke rudarjenja na Pohorju je Teržanova odločno pokazala na potrebo po kemijskih raziskavah kovin, ki naj bi predstav-ljale prvenstveno nalogo pri razreševanju pohorskega rudarstva. Obenem je tudi opozorila na bogate tuje izkušnje s spektralnimi analizami bakra in bakrovih zlitin, kar se zdi zelo umest-no, če pomislimo na zgoraj omenjeni razvoj evropskih arheometalurških raziskav, ki so prav tedaj, v 1980-ih letih, dobivale nov zagon. Pozivu je sledila leta 1984/85 prijava interdisciplinarne naloge na Oddelku za arheologijo ljubljanske Univerze z naslovom "Arheologija okolja in tehnologije". B. Slapšak je tam jasno oblikoval namen in cilj naravoslovnih raziskav v slovenski arheologiji, še posebej tudi raziskav kovine, keramike in stekla, pri čemer je poudaril temeljni pomen vprašanj o izvoru, obdelavi in transportu surovin ter izdelkov. Žal naloga v tej obliki nikoli ni doživela uresničitve. Kljub temu Teržanova ni odnehala in pobuda za načrtne analize kovin ni zamrla. Po prvem mednarodnem kolokviju o bronasti dobi v Sloveniji je bil leta 1987 ob razstavi o bronasti dobi Narodnega muzeja v Ljubljani znova poslan poziv slovenskim naravoslovcem, naj vendar naklonijo svoje strokovno zanimanje tudi raziskovanju preteklosti. Tokrat prizadevanje ni bilo zaman; morda je poma-gala tudi kritika v dnevnem časopisju o naših bronastih pred-metih, ki da so "maček v žaklju", ker zaradi nesodelovanja naravoslovcev arheologi še vedno ne vemo, kateri so bakreni in kateri bronasti.[11] Vsekakor so se za začetek prvih

[8] Za surovce gl. Otto, Witter 1952, 204, 206 in za bakrene predmete gl. *SAM* 2/3 (1968) 10-13, 56-57, 142-143 in *SAM* 1 (1960) 119, 153.

[9] Za analize zlatih predmetov gl. *SAM* 3 (1970) 65, 67-68.

[10] S tem je odprl možnosti nedestruktivnih preiskav površin predmetov n. pr. kositrenja.

[11] I. Popit, Bronasti maček v žaklju, *Delo,* petek, 22. maj 1987, 4. Ob tem naj opozorim še na članek M. Budnarja z Inštituta Jožef Stefan, ki je mesec dni pozneje prav tako v *Delu* kot naravoslovec predstavil zmožnosti metode PIXE za uporabo v arheologiji.

domačih sistematičnih raziskav izkazali kot odločilni dejavniki premišljeno zastavljen izbor gradiva, pravilna izbira metode in odločna osebna zavzetost posameznikov, na prvem mestu B. Teržanove, ki je kot pobudnica raziskav tudi izbrala ustrezno gradivo (depojske najdbe iz pozne bronaste dobe), ter B. Orla, ki je izbral analitsko tehniko (ICP-AES) in našel finančno pot do izvedbe večjega števila analiz. Kajti množičnost analiz, ki jo je bilo zlahka opaziti v tujih raziskavah, se je zdela pogoj *sine qua non* za pridobitev uporabnih domačih rezultatov. Tega pa se ni dalo doseči le s prijateljskim sodelovanjem z raziskovalci v naravoslovnih znanostih, ampak je bilo potrebno najti ustrezen način finansiranja analiz. Izboru gradiva je botrovalo več razlogov. Morda je bila na prvem mestu količina kovinskih izdelkov, ki je v primerja-vi s starejšimi obdobji v Sloveniji največja ravno v pozni bronasti dobi. Iz tega obdobja izvira tudi največje število depojskih najdb, ki so se še posebej zdele primerne za začetek analiz zaradi svoje specifične sestave, ki je obetala zanimive rezultate (to se je pozneje tudi potrdilo!). Večina depojev vsebuje raz-meroma velike skupine istovrstnih izdelkov, ki omogočajo verodostojno, statistično podprto obdelavo in primerjavo rezulta-tov znotraj posamezne skupine in med različnimi skupinami (*sl. 1*). Naš namen je bil dobiti dovolj veliko število sistematično izpeljanih analiz, ki bi jih lahko tudi primerjali z obstoječimi istočasnimi analizami drugod po Evropi. Ker je za ICP-AES- metodo potreben vzorec, so bili izbrani predmeti zaradi velikosti in masivnosti tudi po tej plati primerni za odvzem vzorca; lahko je bilo zakrivati sledove vrtanja (to je odlično opravil Laboratorij za konservacijo Narodnega muzeja Slovenije) in ohraniti primerno veliko količino vzorca za morebitno preverjanje rezultatov.

Tako nam je v letu 1988 gostoljubno odprl vrata Kemijski inštitut v Ljubljani, potem ko se je na vztrajno prigovarjanje B. Orla (Laboratorij za spektroskopijo materialov) in ob soglasju tedanjega direktorja inštituta S. Pejovnika za sodelovanje odločila V. Hudnikova (Laboratorij za analizno kemijo). Razpolagala je z ustrezno analitsko tehniko, ki jo je bila pripravljena vpeljati za raziskave arheološkega gradiva, in strokovno voditi specializante. Direktor Narodnega muzeja (takrat B. Gombač) je privolil na enoletno specializacijo muzejskega sodelavca Z. Milića (sicer vodje Laboratorija za konservacijo in kemika), ki jo je finančno omogočila Raziskovalna skupnost Slovenije - na enak način je namreč tedaj finansirala specializacijo kemikov iz proizvodnje. D. Svoljšak, vodja arheološkega oddelka pa je z veliko mero razumevanja dopustil, da je N. Trampuž Orlova precejšen del svojega časa posvetila seznanjanju z arheo-metalurško problematiko, in da je pozneje kot operativna voditeljica vseh nadaljnjih raziskav lahko tudi poglobila poznavanje te tematike. Ob tem nam več kot naklonjeno ves čas stoji ob strani tudi novi muzejski direktor P. Kos.

Stekle so prve analize, in sicer na gradivu iz depoja Narodnega muzeja Slovenije - konec leta 1989 jih je bilo nekaj več kot sto. Naša skromna začetna želja, da bi spoznali notranjo podobo predmetov, torej sestavo in strukturo njihove kovine, se je začela uresničevati. Prvi rezultati so bili opogumljajoči - v predmetih prvih dveh depojev smo zagledali bakrove zlitine s kositrom, v surovcih pa baker; razlike v vsebnosti kositra so celo kazale na namenske zlitine. Očitna je bila tudi razlika v vsebnosti kositra, ki se je ravnala po tipu in uporabnosti pred-meta. V zlitini za srpe je bilo manj kositra kot v zlitini za sekire, sulice ali meče, zato smo sklepali na namenske zlitine (Trampuž Orel et al. 1991). Nastopil je čas, ko smo lahko raziskave razširili na vse slovenske depoje Ha A in Ha B obdobja (čez 20), kar je pomenilo, da se je moral Narodni muzej s prošnjo za odvzem vzorcev obrniti na več kot deset muzejev v Sloveniji in tujini. Na tem mestu bi rada povedala, da so naši kolegi takoj privolili v sodelovanje, da so z velikim razumevanjem dovolili odvzem vzorcev in fotografiranje predmetov, če je bilo potrebno tudi izposojo gradiva v Ljubljano, in da so s potrpljenjem čakali na rezultate analiz. Zato bi se rada vsem še enkrat zahvalila.

Namen raziskav

Obseg dela, ki je zdaj bil pred nami, je bil velik, zato smo si na podlagi prvih izkušenj jasno opredelili namen. V nasprotju z večino evropskih arheometalurških raziskav, ki so se tedaj (in še vrsto let pozneje) ukvarjale s problemom izvora bakrove rude, smo naše raziskave (zaradi metode, ki nam je bila na voljo in ki omogoča razmeroma hitro izdelavo velikega števila kvantitativnih in kvalitativnih analiz) usmerili v ugotavljanje tehnoloških postopkov - v taljenje kovin, izdelavo zlitin in vlivanje. V naši neposredni sosedščini na Tridentinskem, južnem in severnem Tirolskem ter v Vzhodnih Alpah so se namreč ukvarjali predvsem z odkrivanjem sledov bronastodobnega rudarjenja in taljenja bakrove rude ter z eksperimentalnim taljenjem (Piel, Hauptmann, Schröder 1992; Čierny, Weisgerber, Perini 1992).[12] Po tematiki našim podobne raziskave predmetov so sicer tekle od leta 1987 v Italiji, vendar so vsebovale le metalografske anali-ze (Casagrande et al. 1993; Antonacci Sanpaolo, Canziani Ricci, Follo 1992), zadnje raziskave pa temeljijo na XRF- metodi (Bietti Sestieri et al.1998), katere pomanjkljivost v smislu sistematičnih raziskav smo že omenili. Po tematiki, analitski metodi in obdobju so nam bile najbližje obsežne raziskave bakra in bakrovih zlitin v Švici, katerih rezultati so pokazali, da je mogoče okvirno opredeljevati proizvodna območja kovin-skih izdelkov v Zahodnih Alpah (Rychner 1981; Rychner, Kläntschi 1995). S temi ugotovitvami smo začeli primerjati naše rezultate na jugovzhodnem delu Alp (Trampuž Orel, Klemenc, Hudnik 1993).

Metoda dela

Zaradi možnih preverb izvajanja naših analiz se je V. Hudnikova odločila objaviti ves postopek od jemanja vzorcev, pripra-ve vzorcev in standardnih raztopin, izbora 12 analiziranih elementov (Sn, Pb, Fe, As, Sb, Ni, Co, Zn, Bi, Mn, Ag in Cu), izbire spektralnih črt in meje zaznavnosti posameznih elemen-tov do problemov reprezentativnosti in homogenosti vzorcev (Klemenc et al. 1992). Glede obdelave rezultatov pa se je B. Orel že pri prvih analizah odločil, da bomo analize znotraj posamezne depojske najdbe združili v skupine, ki jih predstav-ljajo predmeti iste vrste - torej analize srpov sledijo analizam sekir, sulic ipd. Na koncu vsake skupine analiz smo dodali seštev-ke povprečnih vrednosti vseh preiskovanih elementov. Pri primerjavi rezultatov smo bili posebej pozorni tudi na kronološko uvrstitev gradiva; tako smo najprej primerjali analize gradiva znotraj iste kronološke stopnje, nato pa smo dobljeni vzorec primerjali z novo kronološko stopnjo. Ker je analizirano gradivo izviralo iz različnih delov Slovenije, smo bili previdni tudi pri morebitnih vplivih geografskih razlik, zato smo vse analize sprva obravnavali le v okviru posameznega najdišča. Na ta način smo dobili boljši pregled nad kemijskimi in arheološkimi značilnostmi posameznih skupin predmetov, laže smo jih primerjali med seboj in z drugimi skupinami, hitreje smo opazili izstopajoče vrednosti. Danes lahko rečemo, da je bil to nov način predstavitve analiz, ki ga do tedaj ni bilo zaslediti v evropskih arheometalurških objavah, vsaj ne v tako dosledni obliki, kot je bilo to storjeno pri naših objavah.[13]

[12] Hauptmann, Marzatico, Perini 1993; Herdits 1993.

[13] Trampuž Orel et al. 1991, t. 2 in 3 ter vse naslednje objave naših analiz.

Cilji raziskav

Ob tako zastavljenem delu je postalo jasno, da bodo analize lahko odgovorile na veliko bolj zahtevna in kompleksna vprašanja, kot je to bilo videti v začetku. Zato smo si zastavili kot cilj odgovore na vprašanja, ki so bila v naslednjih desetih letih vodilo našega raziskovanja:

1. ali je različna sestava zlitin pogojena z: a) različno razvojno stopnjo metalurškega znanja; b) različnim časovnim obdobjem; c) različnim virom surovine; d) različno namembnostjo izdelka;
2. ali je mogoče ugotoviti postopek pridobivanja kovine in izdelave zlitin z analiziranjem polizdelkov (pogač, surovcev in ingotov);
3. ali se da razpoznati mrežo prometnih in trgovskih vezi, v katero je bilo vpeto slovensko ozemlje ob izteku bronaste in v začetku železne dobe, in ali je mogoče ugotoviti, kateremu delavniškemu krogu je pripadalo.

Delo na analizah je v letu 1990 nadaljevala kot magistrski študij S. Klemenčeva,[14] ki je opravila večje število analiz. Nato je v magistrski nalogi[15] ponovno predstavila uporabo ICP-AES-metode za raziskovanje arheološkega gradiva (Klemenc et al. 1992) ter uporabo kemometričnih metod - metodo glavnih osi (PCA) in metodo hierarhičnega grupiranja - za obdelavo velikega števila večdimenzionalnih podatkov.[16] Pridala je tudi tabele analiz, ki jih je opravila (približno 400 analiz iz 11 depojskih najdb), vendar se je podrobneje lotila le interpretacije sestave surovcev (95 analiz iz 7 depojskih najdb). Vsekakor smo lahko zadovoljni, da je arheološka pobuda za analize in izbrano arheološko gradivo služilo za uspešno zaključen magistrski študij s področja kemije, kjer je bilo med mladimi raziskovalci komajda mogoče najti kandidata, ki bi se rajši odločil za raziskovalno delo v povezavi z arheologijo kot pa v kemijski industriji.

Prvi rezultati

V tem obdobju smo nekoliko razširili raziskave predmetov in surovine tudi na metalurško področje.[17] Iz tega časa je poskus metalurške študije pridobivanja bakra na osnovi metalografskih vzorcev surovcev iz Jurke vasi (Paulin, Smolej 1993a; 1993 b). Da bi preverili našo predpostavko o izdelavi srpov iz namenske bakrove zlitine z nizkim kositrom, ki je vzdržala redno brušenje in kovanje rezila (Trampuž et al. 1991), pa smo prosili za sodelovanje tudi M. Doberška. Njegove mikrostrukturne analize treh srpov so potrdile naša pričakovanja - rezilo je bilo kovano; hkrati pa je tudi ugotovil, da so za izdelavo bronaste zlitine za srpe uporabili svež baker, ne pa bron starih, že pretaljenih izdelkov. Odkritje, da so varčni livarji karpatskega obrtniškega kroga uporabljali za srpe namensko zlitino z niz-kim kositrom, je bilo popolna novost glede na raziskave drugih predelov predvsem Zahodne Evrope, kjer so dodajali višje količine kositra in neglede na vrsto predmeta. Tudi ugotovitev, da so bili vsaj nekateri srpi iz depojev uporabljani kot žetveno orodje, je v nasprotju z zelo razširjenim mnenjem, da primarna vloga srpov iz depojev leži v njihovem votivnem ali predmonetarnem pomenu; pa tudi dokaz o uporabi svežega bakra za izdelavo zlitine v pozni bronasti dobi sodi med še maloštevilne ugotovitve, ki podirajo splošno prepričanje, da so v pozni bronasti dobi uporabljali za nove izdelke le pretaljeni bron iz starejših obdobij (Trampuž Orel et al. 1996).

Medtem se je število kemijskih analiz še povečalo; potem ko je mlada raziskovalka V. Kosova dopolnila začeto delo S. Klemenčeve, smo imeli v letu 1995 pred seboj že 928 analiz predmetov iz 23 depojskih najdb, kar je tedaj predstavljalo eno izmed redkih tako obsežnih raziskav na področju predelave prazgodovinskih kovin v Srednji Evropi nasploh in posebej v obdobju pozne bronaste dobe. Vsekakor je za nas tâko število rezultatov predstavljalo problem obdelave, saj je bil pomen uporabe računalniško-statističnih metod, brez katerih si ni bilo mogoče predstavljati relevantnih sklepov dotedanjih raziskav, že nakazan. Razen tega smo potrebovali tudi novega sodelav-ca kemika, ki bi vodil bodoče analize, vendar so mladi slovenski kemiki, razumljivo, videli zase boljše perspektive v farmacevtski industriji kot pa v arheometalurgiji. Položaj je s svojim pristankom na sodelovanje rešil D. J. Heath, doktor kemije okolja, ki se je v letu 1995 priselil v Slovenijo in se pridružil našim raziskavam. Čeprav je bila njegova odločitev eksistencialne narave, se je lotil raziskav s takim raziskovalnim navdušenjem in zanimanjem za arheometalurško problematiko, kakršne-ga ni pokazal noben dotedanji sodelavec. Na podlagi njegovih računalniških obdelav rezultatov in njegove pripravljenosti, da je ob tem prisluhnil tudi arheološki problematiki in zahtevam stroke, je bilo mogoče bolje oblikovati zaključke raziskave prvih šestih let, ki so bili po načrtu B. Teržanove objavljeni skupaj s predstavitvijo vseh depojev in posameznih najdb bronaste dobe v Sloveniji (Teržan 1996; Trampuž Orel, Heath, Hudnik 1996).

Zaključki

Na kratko povzeto - raziskava je odkrila, da je bila sestava bakrovih zlitin v izdelkih iz naših poznobronastodobnih depojev posledica tehnološkega znanja livarjev in odvisna od različnih virov surovin. Za obdobje od 12.-11. st. pr. n. š. (Ha A stopnja) so značilne različne vrste bakrovih zlitin s kositrom, ki so jih livarji skrbno izbirali glede na vrsto predmeta, oziroma da je zlitino narekovala uporaba predmeta. Tako so razlikovali med žilavim in raztegljivim bronom, ki so ga dosegli z dovolj majhno količino bakru dodanega kositra (okrog 4 %) in ki je bil najbolj primeren za izdelavo srpov; srp iz takšnega brona je namreč uspešno prestajal večkratno izmenično brušenje in kova-nje, potrebno za ostro rezilo, ne da bi se zlomil. Po drugi strani pa so izdelovali zlitine z večjo količino kositra (6 % in več), ki so dale trd bron, primeren za udarno orožje in orodje, kot so meči, sulice in sekire, ki je prenesel brušenje, ni ga pa bilo treba kovati, česar višja količina kositra ne bi dopuščala (*sl. 2*). Tako varčno ravnanje s kositrom je prva razkrila prav naša raziskava, ga nato tudi statistično podprla ter ga zaradi ozke tipološke podobnosti naših predmetov hipotetično povezala z izdelki karpatskega obrtniškega kroga (Trampuž Orel et al. 1991).[18] Pozneje je bila

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[14] Magistrski študij S. Klemenčeve je potekal pod mentorstvom V. Hudnikove in v okviru akcije “2000 mladih raziskovalcev”, ki jo je financirala tedanja Raziskovalna skupnost Slovenije, Narodni muzej pa je raziskovalko za določen čas zaposlil.

[15] S. Klemenc, *Študij značilnosti arheoloških predmetov pozne bronaste dobe z ICP-AES in kemometrično analizo* (1993) magistrsko delo, Univerza v Ljubljani.

[16] To je bila zasluga J. Zupana, vodje raziskav na področju kemometrije na Kemijskem inštitutu v Ljubljani, ki je na našo prošnjo naklonjeno sodeloval pri omenjenem magisteriju.

[17] Tu nam prijateljsko, vendar neuradno stoji ob strani že od začetka gospod Ivan Kralj, diplomirani inženir metalurgije, z marsikaterim strokovnim spoznanjem ali nasvetom, ki izvira iz njegovih dolgoletnih izkušenj s področja uporabne metalurgije.

[18] Trampuž Orel, Klemenc, Hudnik 1993; Trampuž Orel, Heath, Hudnik 1996. Isti delavniški krog je bil nedavno definiran tudi s tipološko razvrstitvijo nekaterih srpov (P. Pavlin, Bronastodobni jezičastoročajni srpi z Y- ornamentom, *Arh. vest.* 48, 1997, 27-40).

ta povezava tudi potrjena in sicer je enako tehnološko posebnost odkril Liversage (1995) na osnovi starih stuttgartskih analiz srpov, sekir in mečev iz istočasnih depo-jev IV. in V. stopnje (po Moszolicsevi) v Panonski nižini ob zgornjem toku Tise. Pomembno je, da metalurško tako prefinjenega ravnanja s kositrovimi zlitinami livarji v zahodnih predelih Evrope niso poznali (Craddock 1978; Rychner 1995), kar dodatno dviguje metalurški pomen Karpatskega prostora. Podatek dopolnjuje tudi sliko slovenskega prostora v tem obdobju zadnjih dveh stoletij 2. tisočletja, kot jo je časovno in prostorsko definiral P. Turk z depoji II. horizonta, ki kaže tesne povezave družbenih skupnosti na območju od Furlanije na zaho-du in JZ Transdanubije na vzhodu ter avstrijske Štajerske na severu (Turk 1996). Lahko bi dodali, da so bili prebivalci omenjenega območja tedaj vključeni v gospodarsko in morda tudi politično sfero karpatskega prostora (*sl. 3*).

Upadljivo spremembo v tehnologiji in uporabi surovin je raziskava odkrila na prehodu v 1. tisočletje (Ha A2/Ha B1). V nasprotju s prejšnjim obdobjem, ko v analiziranih predmetih zlitin brona s svincem razen posamičnih izjem takorekoč ni bilo, se zdaj kaže uporaba svinca kot dodatka zlitini že kot značilnost tega časa. Svinec se ne pojavlja v čisti obliki, ampak vedno kot binarna zlitina bakra s svincem ali ternarna zlitina bakra s kositrom in svincem, tako v predmetih kot tudi v polizdelkih, večkrat v presenetljivo visokih količinah. Vsekakor kaže, da so livarji že spoznali vlogo svinca pri kvalitetnejšem vlivanju izdelkov. Da je bila sama tehnologija uporabljana tudi pri nas, dokazujejo številne najdbe delčkov uhatih sekir, zaenkrat predvsem z notranjskih gradišč; te so skoraj vse zlitina bakra z visokimi količinami svinca in so morda služile domačemu livarju kot izboljšava bronaste zlitine (Trampuž Orel, Heath 1998). Množično nastopa tudi nova vrsta metalurških polizdelkov - v kalup vlivani ingoti, ki v nasprotju s preprostejšimi pogačami in surovci že s svojo obliko in načinom izdelave kažejo jasen namen, kako z dogovorjeno zunanjo obliko dati vedeti za nove vrste kovin, ki so jih izdelali. Baker, uporabljen v izdelkih tega obdobja, je povsem drugačne vrste od predhodnega, saj vsebuje visoke nečistoče, med katerimi je po količini vodilen antimon, in ga je mogoče uvrstiti med sulfidne rude tipa Fahlerz. Tu se je pri raziskavah spet pokazalo kot zelo potrebno sodelovanje z geologi (U. Herlec) in metalurgi, kjer se je A. Paulin posebej posvetil razreševanju izdelave novih vrst kovin. Po sestavi nekaterih naših ingotov, ki je bil opredeljen kot "speiss" (D. Heath), sklepamo, da so tedaj izkoriščali ne samo ležišča, bogata s sulfidno bakrovo rudo, temveč celo rudišča s kompleksnimi rudami, ki so vsebovala poleg tetraedrita tudi druge minerale, bogate s kobaltom in nikljem (Paulin et al.1999). Arheološko še ne zadostno raziskana rudišča teh vrst so tudi v naši bližini, v različnih predelih Alp in v srednji Italiji. Razprostranjenost našim izdel-kom najbolj podobnih predmetov, posebno tistih, ki vsebujejo znatne količine svinca,od kolesastih obeskov do uhatih sekir in ingotov, se kaže predvsem v pokrajinah, ležečih zahodno od Slovenije (srednja in severna Italija, Švica). To po eni strani iz več razlogov govori za širjenje tehnološke novosti - uporabe svinca v zlitinah - z Apeninskega polotoka v obrobne dežele na severu in vzhodu - torej tudi k nam (*sl. 4*), po drugi strani pa kaže na skorajda diametralno nasprotno situacijo, v kateri se je znašlo slovensko ozemlje v 1. tisočletju v primerjavi s sta-rejšimi obdobji. Prevladovati so začeli trgovski in družbeni sti-ki, razvidni tudi v tehnoloških novostih, ki so povezovali slovensko ozemlje predvsem z obrobjem severnega Jadrana, s Furlanijo, s Padsko nižino in morda tudi srednjo Italijo na eni strani, in na drugi strani z alpskimi dolinami na severu in zahodu. Enega od pomembnih razlogov novih "zahodno" usmerjenih stikov in verjetno novih prometnih povezav, v katerih vidimo pomembno vlogo doline Soče in njenih pritokov ter idrijskega in cerkljanskega območja, je gotovo predstavljala kovina - in sicer izkoriščanje novih rudišč, tudi takih s kompleksnimi rudami, ter trgovanje kovinami. Tu se zaključki raziskave ujemajo s širšo podobo kulturnih in gospodarskih povezav, kakor jo vidi Teržanova med vzhodnim Sredozemljem in Alpami, ki so zajele tudi zahodnobalkanski prostor in italski polotok v času 11./10 stoletja, in so posredno povezane z iskanjem novih rudišč in širjenjem tehnologije tako bakra kot železa (Teržan 1995; 1996).

Navedeni rezultati raziskav (med katerimi so nekateri vzbudili pozornost tudi v širšem evropskem prostoru) so se nam zdeli dovolj tehtni, da smo se odločili delo nadaljevati (Hänsel 1998; Jockenhövel 1998; Frána et al. 1997). Naše doseda-nje ugotovitve bi radi preverili na gradivu sosednjih geografskih območij in jih tudi soočili s stanjem v drugih kronoloških obdob-jih. Posebno nas zanima tehnološko znanje na koncu mlajše bronaste dobe in v začetku železne dobe, ker utegne biti ključno za celovitejše razumevanje začetkov železarstva na slovenskem ozemlju.

Vsekakor ne smemo ob zaključku tega pregleda spregledati novejših raziskav posamičnih kovinskih predmetov ali predmetov, povezanih s predelavo kovin iz prazgodovinskega obdodja in drugih obdobij, ki so se pojavile predvsem v zadnjih dveh letih,[19] kakor tudi ne arheometričnih raziskav drugih materialov in obdobij, tako jantarja in smol,[20] keramike in stekla[21] ter ka-

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19 Nekatere raziskave so nastale iz konservatorske pobude, kot Z. Milić, J. Rant, I. Nemec, Uporaba nevtronske radiografije pri konserviranju rimskega bodala, *Argo* 40/1, 1997, 135-141; J. Rant et al., *Proc.of the 4th Int. Conf. on NDT of Works of Art* (Berlin 1994) 31-40 in J. Rant et al., *Proc. of the 5th World Conf.* (Berlin 1997) 742-749. Druge so rezultat arheoloških izkopavanj in zanimanja za metalurgijo: Velušček, Greif 1998 ter Šmit, Nečemer 1998. Tretje so v neposredni zvezi z raziskavami poznobronastodobnih depojev na Slovenskem (D. J. Heath, N. Trampuž Orel, Visual properties of prehistoric alloys: analyses of copper based artefacts by ICP-AES, v: *11. medn. konf. Spectroscopy in theory and practice, Bled, 11.-15. 4. 1999, Book of abstracts,* 89. Iste raziskave so spodbudile k samostojnim obravnavam gradiva tudi sodelujoče slovenske metalurge: Paulin, Herdits 1996; Paulin et al. 1998; M. Doberšek, A. Paulin, *Kovine, zlitine, tehnologije* 32, 1998, 99-103; Paulin 1998; 1999 - obravnave so potrebne arheološkega komentarja! Tečejo tudi raziskave zgodnjesrednjeveških kovinskih predmetov (sodelovanje Narodnega muzeja Slovenije in Inštituta Jožef Stefan v Ljubljani).

20 Hadži, Cvek 1976; J. Puš, Premazi in smolnati kit na prazgodovinskih posodah, *Arh. vest.* 27, 1976, 124-127; Hadži, Orel 1978; o metodah in rezultatih teh raziskav tudi Trampuž Orel 1990.

21 M. Daszkiewicz, G. Schneider, Chemical, mineralogical and technological studies of fabrics of Roman vessels and lamps from Poetovio, v: J. Istenič, *Poetovio - zahodna grobišča.* Kat. in monogr. (1999) (v pripravi za tisk); I. Klopčić, Mineralogical research on the neolithic ceramic assemblage from Moverna vas, v: *Recent Developments in Yugoslav Archaeology,* BAR Int. Ser. 431, 1988, 201-209; M. Novič, M. Novič, J. Zupan, B. Križ, Chemometric evaluation of the ICP-AES analyses of archaeological samples, v: *11. medn. konf. Spectroscopy in Theory and Practice, Bled, 11.-15. 4. 1999, Book of abstracts,* 147; omenjena raziskava se mogoče navezuje na začetke analiz novomeškega gradiva, prim. M. Novič, *Vzorčevanje in elektrokemijska analiza arheoloških zlitin iz obdobja žarnih grobišč* (1979) dipl. nal., FNT Ljubljana) ter Ž. Šmit, P. Pelicon, G. Vidmar, B. Zorko, M. Budnar, P. Kump, M. Nečemer, Analysis of Medieval Glass by Proton Induced X-ray Emmission Spectroscopy, v: *11. medn. konf. Spectroscopy in Theory and Practice, Bled, 11.-15. 4. 1999, Book of abstracts,* 107.

menih orodij,[22] pa tudi dendrokronoloških in magnetometričnih raziskav,[23] med katerimi tečejo tudi sistematične raziskave.

Pomen arheometalurških raziskav

Pregled dosedanjih raziskav je pokazal, da je bil vsebinsko večji del slovenskih raziskav kovin (pa tudi drugih materialov) usmerjen na posamične predmete in neposredno reševanje vprašanja, ki ga je navadno predstavljala neznana sestava kovine ali druge snovi. Te sicer uspešne raziskave so nedvomno prispevale zadovoljive odgovore v zaključenem obsegu, in so se tudi izkazale kot obvezne za dopolnjevanje "osebne izkaznice" arheološkega predmeta in kvalitetno konservatorsko obde-lavo gradiva, niso pa imele večje teže pri boljšem poznavanju kompleksne podobe slovenskega prostora v arheoloških obdob-jih nasploh in v prazgodovini posebej. Vendar pa so utrle pot k spoznanju, da je potrebno za dosego tega cilja zasnovati sistematične raziskave, ki jih slovenski znanstveni potencial in siceršnja visoka tehnična opremljenost slovenskih naravoslovnih inštitutov omogočata. Seveda ni mogoče pričakovati, da bi kljub tako kvalitetni podpori naravoslovnih znanosti raziskava dala uspešne zaključke brez premišljenega arheološkega načrta. Arheometalurška problematika je kompleksna in presega meje slovenskega ozemlja, zato je potrebno naravoslovnim sodelavcem, ki pri nas (še) niso šolani interdisciplinarno, pomagati pri seznanjanju z ustreznimi arheološkimi raziskavami. Po-goj za dobro zasnovano delo je jasno definirana arheološka problematika, ki je zastavljena v okviru celotnega slovenskega prostora, v skladu z njo pa premišljeno izbrano, številčno obsežno gradivo iz arheološko dobro opredeljenih kontekstov. K temu sodi optimalna analitska metoda in ustrezno zasnovana interdisciplinarna raziskovalna skupina, v kateri morajo arheologi ena-kovredno in aktivno sodelovati z naravoslovci pri obdelavi in interpretaciji rezultatov. Poudariti je treba, da je v preteklih letih Ministrstvo za znanost in tehnologijo republike Slovenije prisluhnilo tovrstnim prizadevanjem in se mu zato na tem mestu ponovno zahvaljujemo. Leta 1998 je tudi odprlo možnost finansiranja interdisciplinarnih raziskav s področja humanistike in naravoslovja, kar bo, upajmo, prispevalo k širjenju sistematičnih arheometričnih raziskav, med njimi tudi arheometalurških. Korak k temu je nedavna ustanovitev Centra za terenske raziskave, ki ga vodijo osrednje slovenske arheološke ustanove - Inštitut za arheologijo Znanstvenoraziskovalnega centra Slovenske akademije znanosti in umetnosti, Oddelek za arheologijo Filozofske fakultete v Ljubljani in Narodni muzej Slovenije.

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[22] S. Petru, Metode preiskav sledov uporabe na kamenih orodjih iz najdišč Zakajeni spodmol in Mala Triglavca. *Por. razisk. pal. neol. eneol. Slov.* 24, 1997, 79-97; Ž. Šmit, S. Petru, G. Grime, M. Budnar, T. Vidmar, B. Zorko M. Ravnikar, Usewear-induced deposition on prehistoric flint tools, v: *Nuclear Instruments and Methods in Physics Research* B 140 (1998) 209-216.

[23] B. Mušič, L. Orengo, Magnetometrične raziskave železnodobnega talilnega kompleksa na Cvingerju pri Meniški vasi. - *Arh. vest.* 49, 1998, 157-186; K. Čufar, T. Levanič, A. Velušček, Dendrokronološke raziskave na koliščih Spodnje mostišče 1 in 2 ter Hočevarica. - *Arh. vest.* 49, 1998, 75-92.