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METALLURGY OF COPPER IN THE CONTEXT OF METALLOGRAPHIC ANALYSIS OF ARCHEOLOGICAL MATERIALS EXCAVATED AT THE MARKET SQUARE IN KRAKOW

METALURGIA MIEDZI W KONTEKŚCIE BADAŃ METALOZNAWCZYCH ZABYTKÓW ARCHEOLOGICZNYCH Z RYNKU GŁÓWNEGO W KRAKOWIE

The paper looks at the history of copper exploitation and smelting from ancient times. Historical background serves the purpose of presenting research issues associated with archaeological samples gained through excavations at the Market Square in Krakow, that is semi-products deriving from the copper and ore recovery process. Copper imported from the area of the present-day Slovakia was given the greatest importance in medieval Poland. Krakow then played a key role in the European copper trade. In the 15th century, a copper smelter in Mogila near Krakow handled raw copper rafination. Availability of raw materials enabled rapid development of foundry.

Traces of activities associated with metal (mostly copper and lead) preparation for trading and production date back to the 13th century; the peak period was the 15th century. The said materials expand the database of metallographic analysis of archaeological materials and provide opportunities for comparison of local finds with domestic and European collections; this in turn will contribute to better understanding of old metallurgical and foundry processes.

Keywords: copper, archaeometallurgy

Praca przybliża zagadnienia związane z eksploatacją i wytapianiem miedzi od czasów starożytnych. Tło historyczne służy przedstawieniu kwestii badawczych związanych z materiałem archeologicznym pozyskanym, w ramach prac wykopaliskowych na Rynku Głównym w Krakowie, w postaci półproduktów z procesu otrzymywania miedzi z rud.

W Polsce w okresie średniowiecza największe znaczenie miała miedź importowana z terenów Słowacji. Kraków wówczas odgrywał wielką rolę w handlu miedzią w skali europejskiej. W XV wieku działała huta miedzi w Mogile pod Krakowem, w której następował proces rafinacji miedzi surowej. Dostępność surowca była jednym z czynników umożliwiających szybki rozwój odlewnictwa.

Na Rynku w Krakowie ślady działalności związanej z przygotowaniem metalu (głównie miedzi i ołowiu) do handlu i produkcji pojawiają się od XIII wieku, a nasilają w wieku XV. Posiadany materiał pozwoli wzbogacić bazę analiz metaloznawczych zabytków archeologicznych i poszerzy możliwości porównania miejscowych znalezisk z krajowymi i europejskimi zbiorami, co przyczyni się do lepszego rozpoznania dawnych procesów metalurgicznych i odlewniczych.

1. Historical approach to copper

Copper is one of the oldest metals known to humanity. The first information of copper obtained from malachite, was confirmed in Anatolia, in the present day Turkey, nearly 6200 years B.C. The first copper products discovered at the South of Europe originated approximately 4800 years B.C. [2].

Copper deposits on Cyprus, called by Romans the Cyprus Stone was very important in ancient times. This is also an origin of the Latin name of copper: *cuprum*. Older Pliniusz (23.-79 year A.C.) in his book *Natural History*, being a prototype of systematic encyclopaedia, wrote that a copper ore was discovered in Cyprus by Cynyras, Agrypa's son, while a method of its *melting and preparation* was done by Scytes from Lidia or Delas, citizen of Frygia. During the Pliniusz times, copper was melted in shaft furnaces where its ore was remelted and roasted several times. The final effect was reduced metal, flowing to a container from a drain hole. The basic metallurgical fuel was that time a charcoal [5].

Development of copper excavation caused a versatile application of bronzes. Various kinds of copper alloys were used already in ancient times. Pliniusz mentioned,

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among others, Corinthian bronze, (copper, gold and silver alloy), *hepatizon* – bronze from Delft used by famous Greek sculptors Myron and Polyktet and bronze form Egina. However, he emphasized an importance for casting of bronze from Campania (tin-lead bronze). He also mentioned an existence of brass and noticed that bronze products are often corroding and recommended covering such products by olive or liquid tar for their protection [5].

The oldest copper products found in the Polish territory are from 3700-3500 years B.C. (copper epoch). Probably they were produced on the spot from raw materials brought from Transylvania or Easter-Alp centres. Polish antiques from the bronze epoch indicate contacts with the excavation and processing copper centres in the territories of the present day Czech Republic and Germany. That time, copper ores were also excavated in the vicinity of Legnica and Złotoryja, which enabled operations of several local casting workshops [2].

As the results of archaeological excavations fragments of clay crucibles, nozzles and copper products have been found in this region. A significant group of the earliest copper products constitutes tools and armaments (picks, axes and swords) as well as ornaments (bracelets, armlets, ear-rings, rings, hangers) and also objects related to religious cults [3].

Lead melting is also connected with a copper production. A development of metallurgical methods allowed melting various polymorphous ores. Components were separated in final treatments. Lead and copper ores often contained significant amounts of silver, which was recovered. Old mining and metallurgical centres in the Central Europe were localised in regions of Lower and Upper Hartz, Upper Saxony, Touring, Tyrol, Karintia and in territories of Czech, Moravia, Slovakia and Transylvania. History of exploitation and production of metals in Poland is connected with Kraków and Upper Silesia Region, Lower Silesia, Świętokrzyskie Mountains, Tatra and Carpathians [1].

2. Cooper production and trade in Poland

In the middle ages, copper imported from Slovakia territories – being the part of Hungary – was the most important in Poland. It was intensely produced in seven mining towns, the largest being: Banska Štiavnica, Banska Bystřica and Kremnica. Copper constituted the main trade object of Krakow, reaching European harbours via Krakow merchants. Kraków belonged that time to the Hanzeatic Association, the most powerful trade organization. In the characteristics of fourteen the most important towns of this organization Kraków was named *ein Kupfer-Haus* i.e. a Copper House. Another product – listed in custom rates – which was reaching European markets, via Kraków, was Polish lead.

Local ores were also exploited in Poland. Lead, zinc and silver ores were found within Kraków and Upper Silesia Region. We have reliable information that in the first half of the XIV century mining of copper ores was done in Miedzianka in Lower Silesia. Deposits of copper ores were discovered near Chęciny in the second half of the XV century and in the year 1487 salt-mine-man Jan Karaś opened the first copper plant in Polichno village [4]. The copper plant operated already in the XV century in Mogiła near Kraków, in which Jan Turzo was refining crude Hungarian copper and probably obtaining silver from this ore by means of a new method (*Saigerkunst*). At the end of the XVI century the exploitation of ores in Kraków bishops' lands in Miedziana Góra was undertaken. The metallurgical plant was operating in the XVII century in Białogon, where copper, lead and silver were obtained [1].

Availability of raw materials enabled a fast development of casting practice. In medieval and renaissance Kraków small casting workshops were operating, producing elements of costumes (buckles, belt ferrules), jewellery and religion cult objects – from bronze. Some crucibles and parts of casting moulds found from time to time in various parts of Kraków witness their activities. Smart bell-founder masters worked here and created impressive products such as – not existing any more – the oldest in Małopolska bell from Krasocin with engraving: "Kracov me fecit", 1270, as well as bells for the Mariacki Church and Wawel Cathedra, baptismal fonts and sepulchral stones. Bell-founders were called - in medieval sources – *cuprifusores*, *rufifusores*, and also *rotgissers*, what corresponded to a red colour of copper. They belonged to the same guild as tin-founders, bronze-founders and braziers in the XIV century. They produced various decorative as well as everyday use products and also liturgical equipment for secular and clergy clients. High quality of the products indicated mastering of difficult casting art and this – in turn – manifested well being of workshops and an appreciation among people. Guild members were often appointed to municipal posts [6].

3. Cooper metallurgy

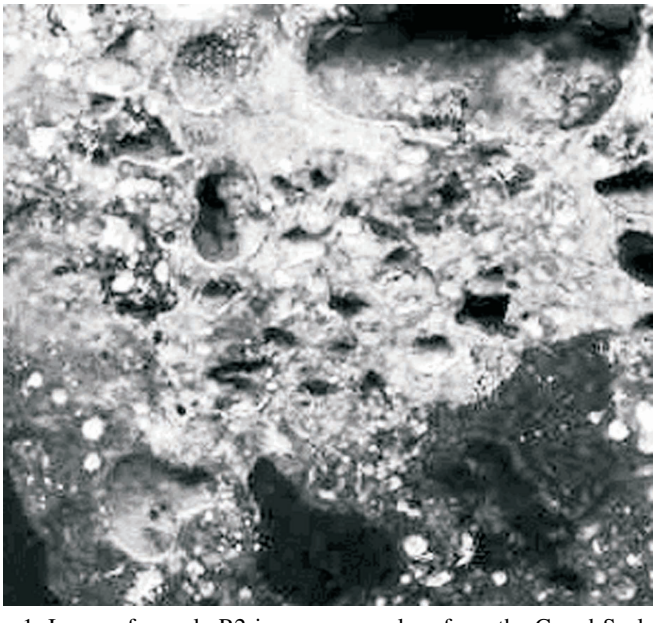
Copper metallurgy was mainly based on sulphide ores. Due to a technological progress in the Central Europe, from the XV century, not only copper, but also silver and gold was obtained. Ores were melted in shaft furnaces using fluxing agents, mainly silica. The so-called *raw stone* was obtained, in which a copper content was within the range of 10-60%, depending on an ore com-

position and a degree of roasting. Raw stones contained also sulphur and iron. It was further repeatedly roasted in order to remove sulphur completely. After those operations (repeated roasting and melting) a stone enriched with copper – called *copper stone* was obtained. As a result of further processes the so-called *black copper*, requiring purification was obtained. Multistage character of this process was due to attempts of recovering silver contained in ores.

If copper ores contained increased amounts of silver, at the very beginning of the process, lead was introduced to combine with silver flowing from a furnace [1]. Silver leftover was remaining in black copper. This copper metallurgical method consisting of melting into stone, roasting and then reducing melting became popular in Europe, and is described in written sources from that time.

Archaeological investigation in the Main Market Square in Kraków, at the southeast side of Sukiennice (the Cloth Hall), indicated an existence of small fragments of copper, lead and iron, dated to the XIII century. They proof, that already in this time the institution – called the Grand Scales – related to the raw materials trade was functioning in Kraków. The highest amounts of metal parts – in the Scales building – were found in the XV century layers. In one of the rooms – with a furnace leftover – more than 1500 metal elements were found. Archaeological works and metallographic tests allowed discovering, apart from pure metals (copper and lead), various objects, which should be treated as intermediate products of the copper melting process.

As an example two characteristic, but quite different, architectural monuments marked by symbols: R2 and R5, found in room R in the layer dated to the XV century – were selected from a large group of objects. Already an observation of samples in a macro scale allowed noticing variability of their structure (Fig. 1 -2).



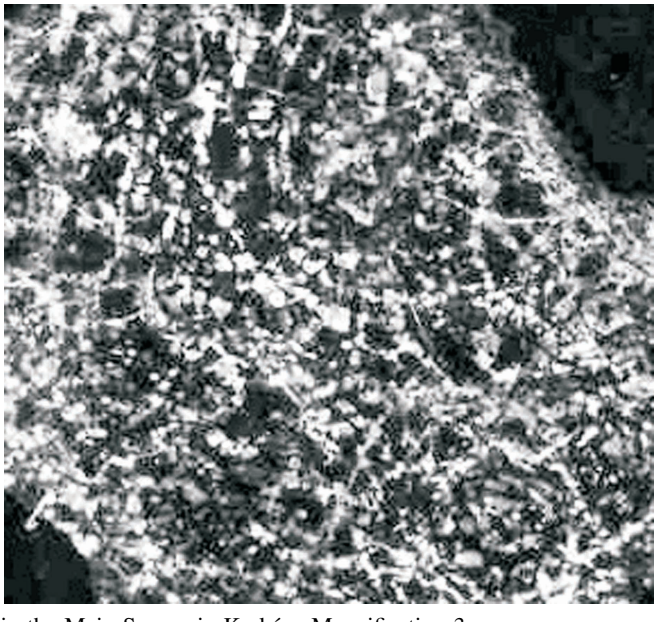


Fig. 1. Image of sample R2 in a macro scale – from the Grand Scales in the Main Square in Kraków. Magnification 3 x
Fig. 2. Image of sample R5 in a macro scale – from the Grand scales in the Main Market Square in Kraków. Magnification 3 x

Metallographic tests confirmed differences in a chemical composition and in shape and phase distribution in samples taken from the investigated material (Fig. 3-9).

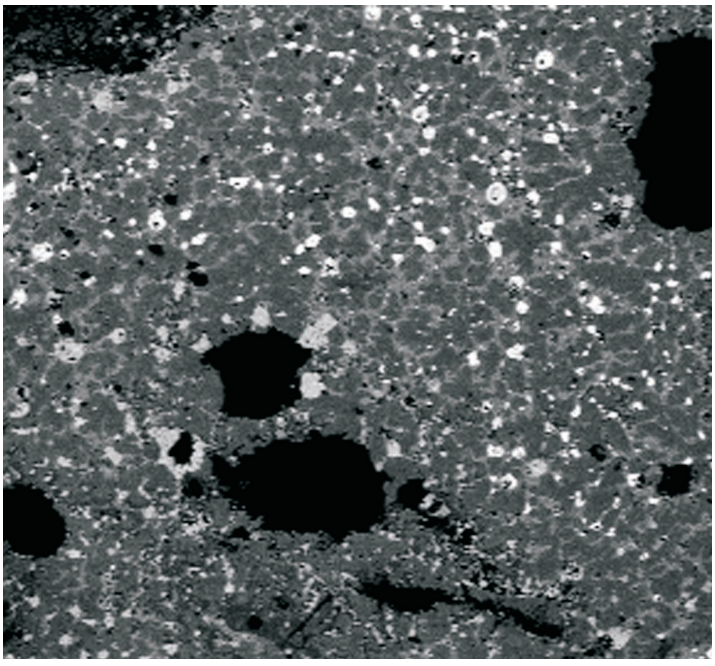


Fig. 3. SE image of sample R2 from the Grand Scales in the Main Market Square in Kraków. Magnification 50 x

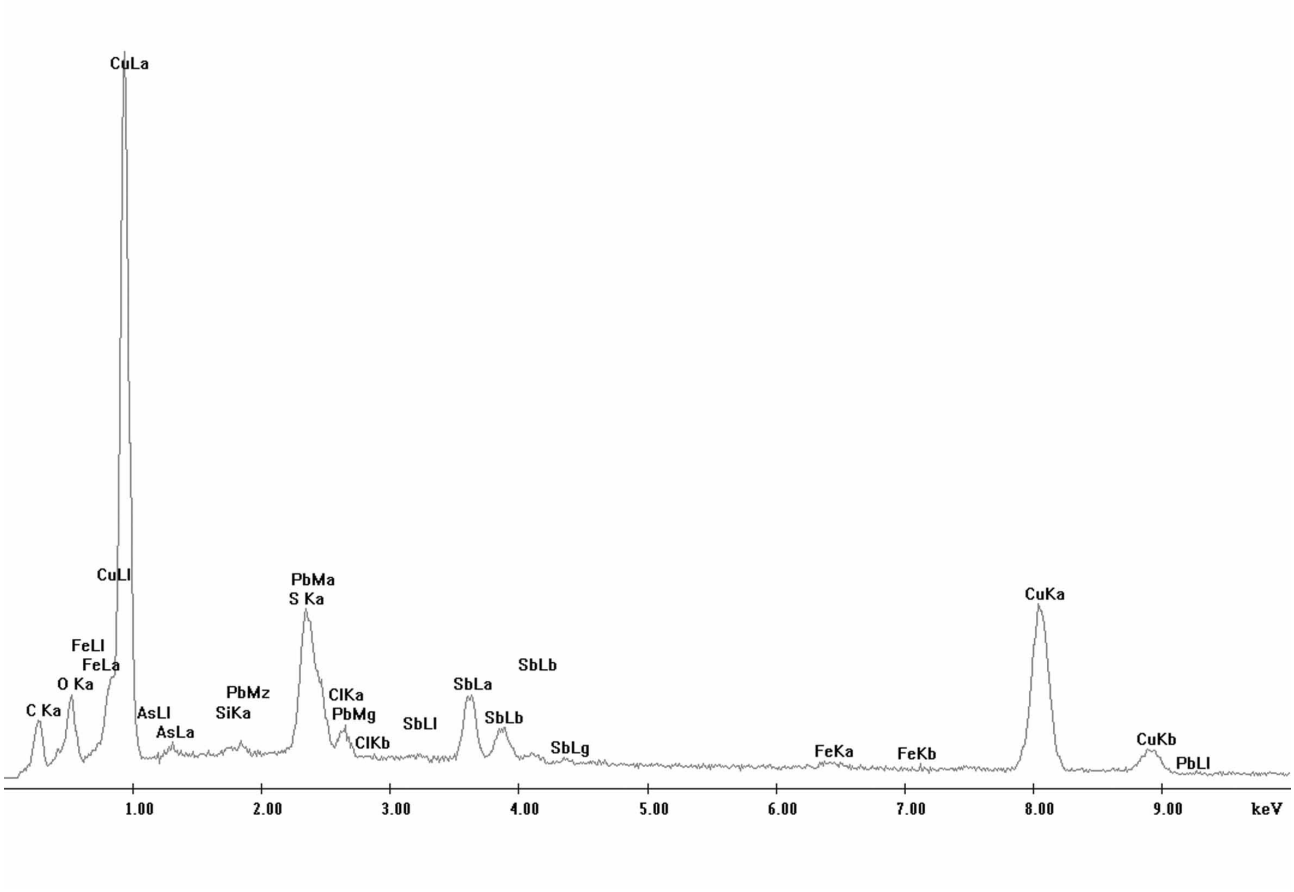


Fig. 4. Fluorescent X-ray spectrum of sample R2 from the Grand Scales in the Main Market Square in Kraków

Analyses indicated that copper dominates in a chemical composition of the tested sample. Lead, iron, antimony, arsenic, sulphur and silica were also found.

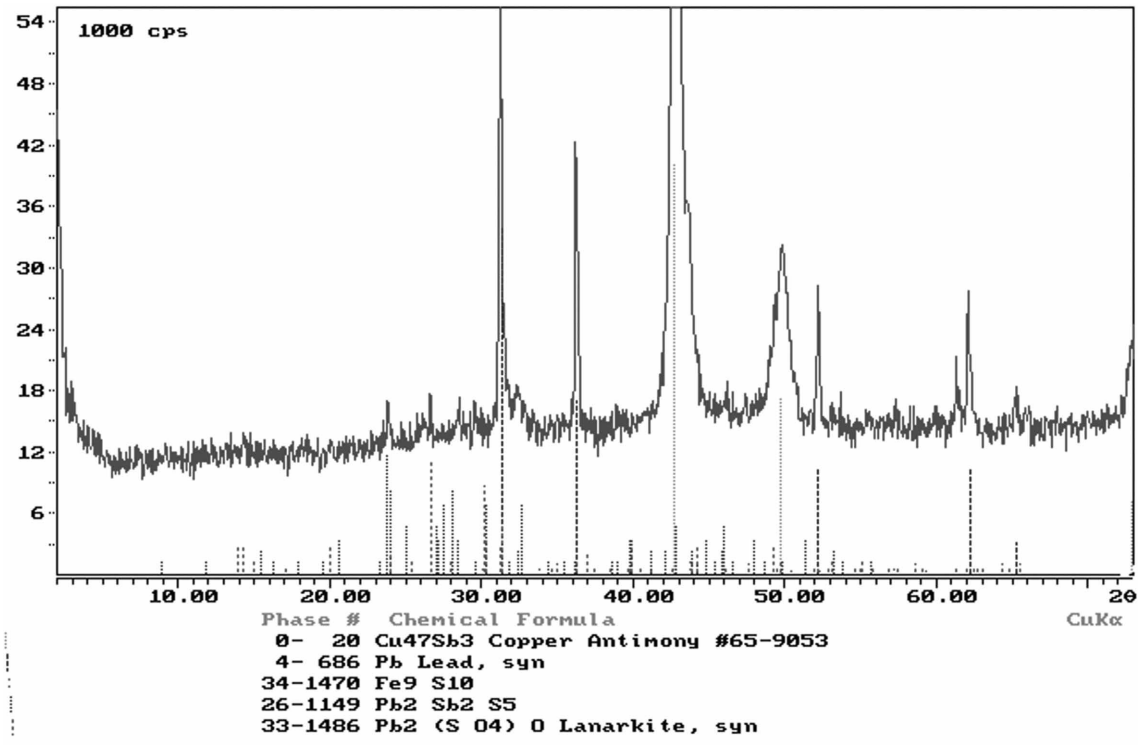


Fig. 5. X-ray diffraction pattern of sample R2 from the Grand Scales in the Main Market Square in Kraków

On the bases of investigations performed by means of the X-ray diffractiometer in sample R2 the presence of compounds of sulphur with iron and with antimony and lead (Fig.5) – was found. Lead was also seen as precipitates (light phase). Copper was present in inter-metallic compounds together with antimony.

Sample R5 was also of a multiphase built, which is shown in a scanning microscope spectrum (Fig.6).

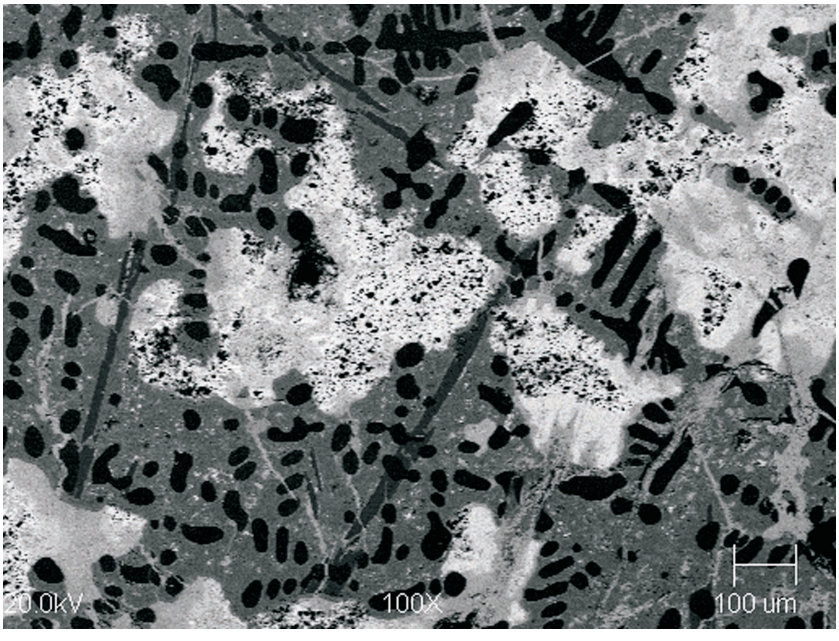


Fig. 6. SE spectrum of sample R5 from the Grand Scales in the Main Market Square in Kraków. Magnification 100 x

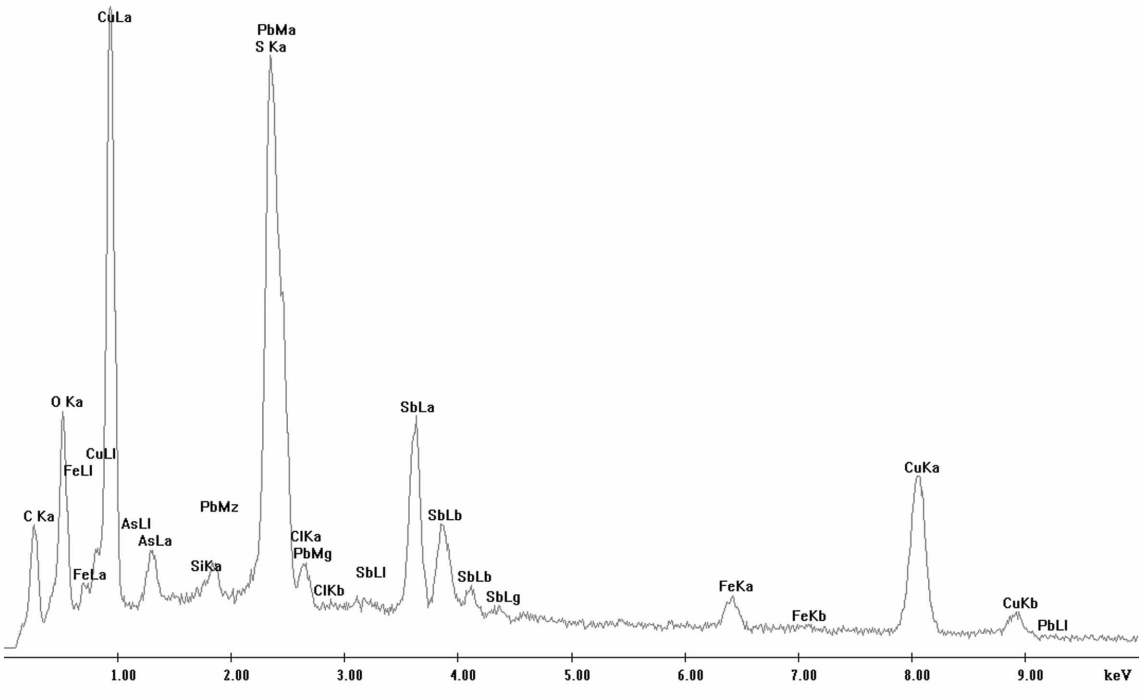


Fig. 7. Fluorescent X-ray spectrum of sample R5 from the Grand Scales in the Main Market Square in Kraków

Sample R5 is characterised by a different chemical composition, higher sulphur content. Sulphur is accompanied by several elements such as antimony, lead, iron, arsenic and silica.

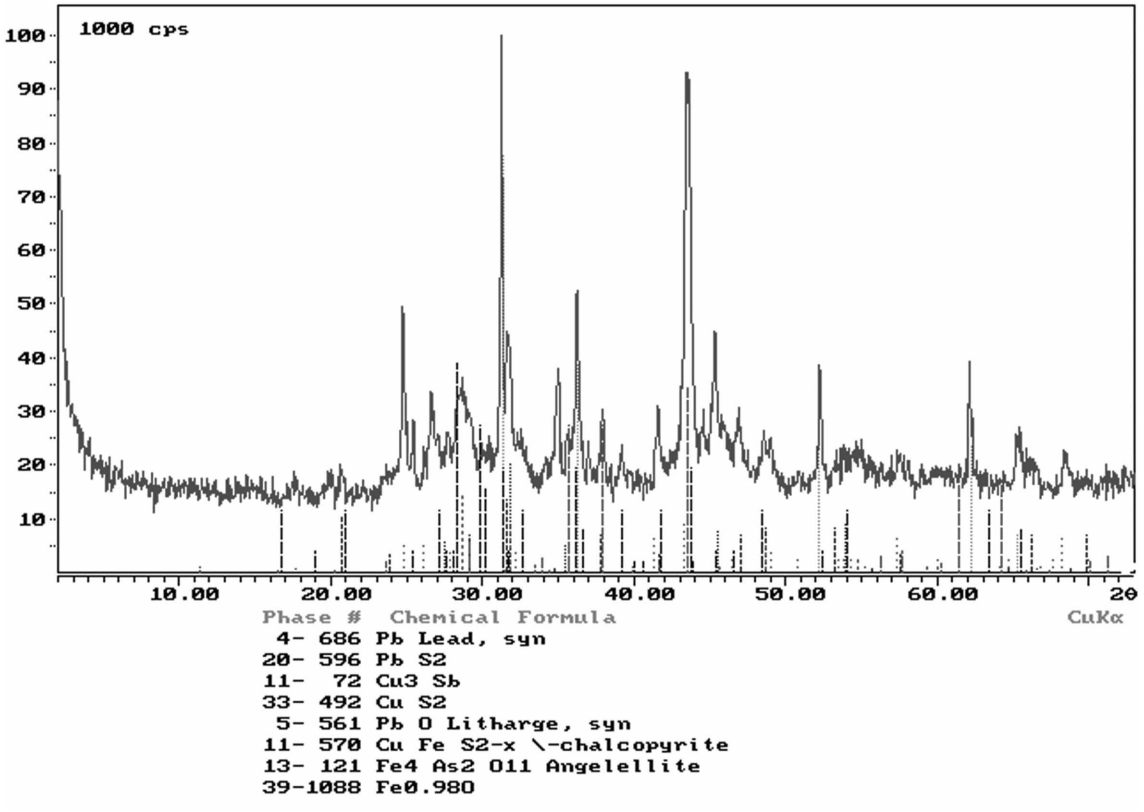


Fig. 8. X-ray diffraction pattern of sample R5 from the Grand Scales in the Main Market Square in Kraków

X-ray diffraction pattern (Fig. 8) allowed identifying phases being components of sample R5. Sulphur occurred in formula with copper, lead and iron and copper. Copper was present as inter-metallic compound with antimony as well as in a form of sulphide.

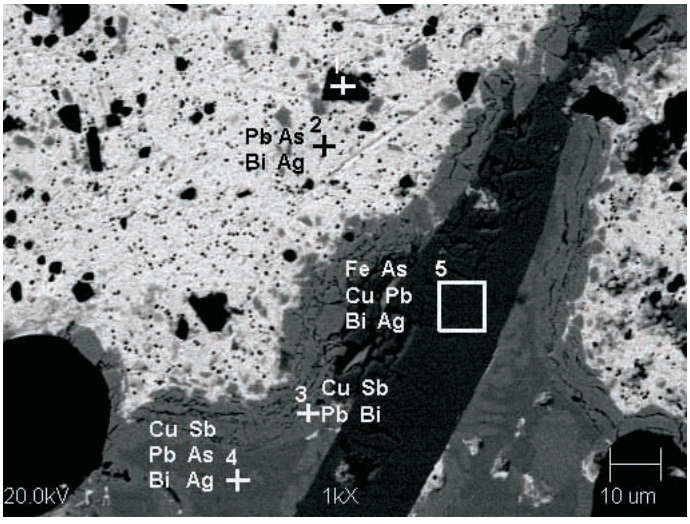


Fig. 9. SE spectrum, X-ray microanalysis of sample R5 from the Grand Scales in the Main Market Square in Kraków. Magnification 1000 x

Examinations of samples were performed by means of the fluorescent X-ray analysis in micro regions. Chemical compositions of individual phases were determined on these bases (Table 1). A light phase contains high lead and arsenic concentrations as well as other elements in much smaller amounts: bismuth, silver, antimony and iron. A grey phase contains mainly copper and antimony and the remaining elements are in negligible concentrations. A dark phase consists mainly of iron and arsenic, and much smaller amounts of copper and lead. Fine black precipitates indicate the presence of charcoal and silica.

TABLE 1

X-ray microanalysis analysis for sample R5 from Grand Scales in Kraków (for Fig. 9)

Zone/point	Element concentration (% by weight)										
	Cu	Pb	Sb	As	Fe	Bi	Ag	S	Si	Sn	C
1	–	–	–	–	–	–	–	–	44.86	–	55.12
2	0.67	74.07	0.45	20.96	0.51	2.21	0.53	–	0.16	0.44	
3	47.13	2.59	47.78	0.56	0.66	1.12	0.06	–	0.11	0.00	
4	58.71	3.36	34.15	1.48	0.25	1.14	0.63	0.07	0.24	0.00	
5	14	5.33	1.04	33.19	43.63	2.05	0.29	0.15	0.05	0.56	

To compare samples and to visualise their differences the average approximated distribution of elements is given in Table 2.

TABLE 2

Average approximated distribution of elements in the selected samples [% by weight]

Sample	Element concentration (% by weight)								
	Cu	Pb	Sb	As	Fe	Bi	Ag	S	Si
R2	72.94	5.84	10.09	0.86	0.35	1.77	0.19	1.65	6.29
R5	39.33	19.95	21.00	11.85	3.30	0.28	0.19	2.87	1.23

Metal elements found in archaeological excavation in the Grand Scales area in the Main Market Square in Kraków can indicate an active trade and craftsmen operations in this medieval and renaissance town.

Examinations allowed observations of samples being witnesses of old metallurgical processes, which were performed in metallurgical plants and in the last phases probably also on the spot near the Grand Scales within the *melting workshops*, which were mentioned about in documents from the times of the king Kasimir the Great. The examined samples, out of which only two characteristic ones were shown in the hereby paper, were highly heterogeneous both in a micro and in a macro scale. Simultaneously they exhibited the different structure, chemical composition and also shape, kind and distribution of precipitates. Fluorescent X-ray analysis, in micro zones, allowed for the qualitative and quantitative determination of the presence of chemical elements in individual phases. Significant differences in contents of all elements – apart from silver – were seen at the average distribution. The largest differences are in copper, lead, antimony and arsenic concentrations. The presence of sulphur and arsenic in those ancient discoveries indicates quality imperfections of materials. Also silica, antimony and large amounts of other elements should be treated as contaminations. However, a relatively high percentage of silver, which remains at the level of 0.19% – by weight (in a micro zone it reaches even 0.63% – by weight) and copper in metal historical elements can confirm that these materials were intermediate products prepared for a further treatment leading to the silver recovery and copper refining.

The collected results will enrich the analytical basis of metallic historical monuments and broaden the possibility of comparing them with other domestic or imported archaeological objects, what should contribute to better recognition of old metallurgical and casting processes.

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