Nanotechnology for Environmental Engineering (2022) 7:965–972
https://doi.org/10.1007/s41204-021-00200-6

ORIGINAL PAPER

# Application of X-ray nano-CT fluoroscopy and fluorescence spectroscopy in the study of ancient bronzes

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Received: 21 October 2021 / Accepted: 1 December 2021 / Published online: 2 February 2022


**Abstract**
Nanotechnology is defined as design and production of structures, devices and systems by controlled manipulation of sizes and shapes at atomic, molecular. Through X-ray nano-CT, we have scanned archaeological artifacts that cannot be observed by human eyes without damaging cultural relics, so as to better study and restore protected cultural relics. The principles of X-ray fluoroscopy and fluorescence spectral analysis were introduced, which can obtain information about the internal structure, manufacturing process and erosion of cultural relics. These two techniques were applied to the detection of some bronzes in Shang and Zhou dynasties, and the detection images and data of two bronzes in Shang Dynasty were given. The preservation, casting process and alloy composition were analyzed and discussed. It is determined that the ware is cast by the mud block model method. The discussion and analysis tend to support that the alloy technology originated from the typical ternary alloy system in Shang and Zhou dynasties. During this period, craftsmen have summed up a set of scientific bronze alloy system.

**Keywords** X-ray fluoroscopy · X-ray fluorescence spectroscopy · Bronzes · Nondestructive testing

## Introduction

Traditional archaeology, especially artifact archaeology, mostly adopts the methods of stratigraphy, artifact typology, textual research and chronology to study the authenticity, age, place and other information of the research object and reveals the social relations at that time. These methods are intuitive, economical and convenient and still occupy a major position in today's archaeology, especially in Chinese archaeology. However, their shortcomings are also obvious: too much reliance on experience, too much subjective judgment, inability to accurately determine the age of objects, and so on. Since the twentieth century, the ideas and methods such as carbon-14 dating, X-ray nondestructive testing, lead isotope testing and Raman spectral analysis have gradually matured and applied to the field of traditional archaeology with the continuous emergence and development of new scientific and technological means. It has brought new academic vitality to it and formed a new branch of archaeology, including scientific and technological archaeology. More and more scholars, such as Mei Jianjun [1], Jin Zhengyao [2] and Wu Xiaohong [3], begin to pay attention to and use scientific and technological means to carry out archaeological research. However, as far as China is concerned, the existing and newly released archaeological materials are very rich, and so far only a small number of them have used modern science and technology for research. Scientific and technological archaeology provides new ideas, new methods and new equipment, weakens the influence of personal subjective factors in research and gradually makes breakthroughs and improvements in qualitative and quantitative research compared with traditional archaeological methods. It can be predicted that the significance of scientific and technological archaeology using a variety of modern scientific and technological ideas and means will become more and more important in archaeology.

X-ray nano-CT fluoroscopy and fluorescence spectrum analysis are more mature modern technologies. We can get a lot of information about the internal structure and element content of cultural relics without causing any damage to cultural relics by using X-ray perspective and fluorescence spectrum analysis technology to detect cultural relics. This technology has been applied in the internal structure

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detection of cultural relics. Bronze ware is a symbol of ancient Chinese civilization. Using the above-mentioned modern science and technology to study the bronzes of the Shang and Zhou dynasties to obtain intuitive and scientific evidence is of great significance to the textual research of its age, origin, production technology, social exchanges and its protection and restoration.

## Technical principle and its application in archaeology of artifacts

Cathode-ray tubes are still the most practical way to obtain X-rays of sufficient intensity, that is, bombarding the anode with high-speed electrons at high voltage since Roentgen discovered X-rays (Fig. 1). X-ray can penetrate matter, and the energy attenuates in the process of penetration. Its penetration ability and the degree of absorption by the material are related to the attenuation coefficient μ, uniformity E and thickness h of the material. As a consequence, the amount of radiation reaching the screen or X-ray film after penetrating the material is different, forming images with a different black and white contrast (Fig. 2). The current preservation and detailed features of each cultural relic are unique. According to the X-ray film of the cultural relic, a lot of valuable information can be read and deduced, such as the degree of damage to the objects, subcutaneous corrosion, internal structure technology, rust covered patterns and inscriptions and restoration status. In addition, this important information that we cannot see with the naked eye can help us to see some technical, artistic and historical features. In addition, the nondestructive detection of X-ray fluoroscopy is particularly important for the research and protection of cultural relics.

The inner electrons resonantly absorb the radiated energy of rays and make a transition, leaving a vacancy, and the outer electrons in the high-energy state transition to the electron vacancies in the inner layer and release the excess energy in the form of X-rays when X-ray irradiates matter, if the energy of X-ray is in the same order of magnitude as the energy of electrons in the inner layer of matter atoms, which

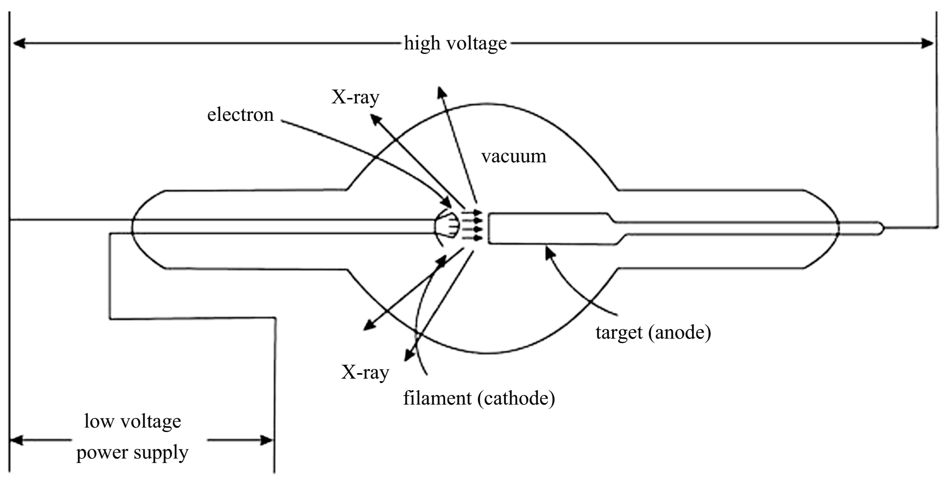


**Fig. 1** The generation principle of X-ray

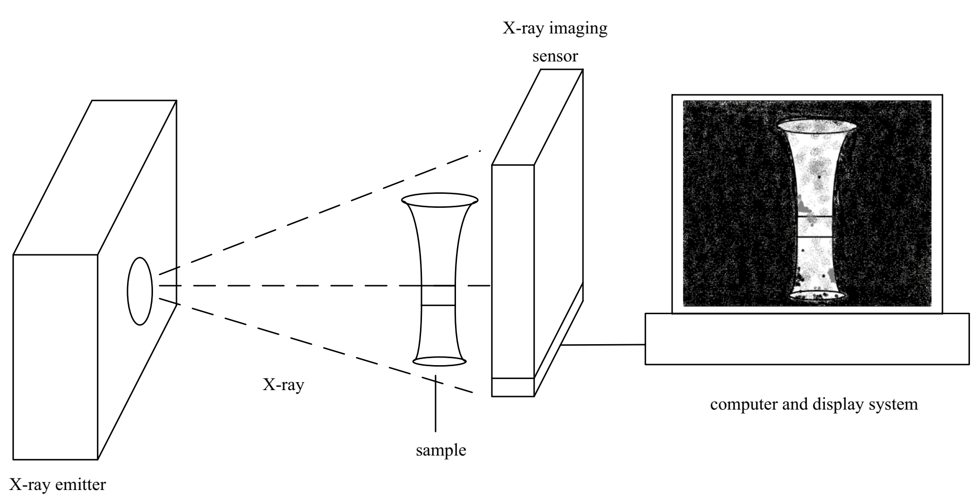


**Fig. 2** The diagram of X-ray fluoroscopy

is called X-ray fluorescence (XRF). The energy of fluorescence is equal to the transition energy between atoms. The specific electron transition energy of different element atoms is different, and the wavelength of fluorescence produced by X-ray irradiation is also different, so the type of elements contained in the material can be determined according to the wavelength characteristics; the higher the content of a certain element, the greater the fluorescence energy intensity, that is, the fluorescence intensity. As a consequence, the content of the corresponding elements can be calculated. For example, if the sample contains two elements A and B, and the content of A is higher, the fluorescence wavelength of the two is different, and the fluorescence intensity of A is higher (Fig. 3).

Specifically, the wavelength and atomic number Z conform to Moseley's law:

$$\sqrt{\frac{1}{\lambda}} = k(Z - S) \tag{1}$$

where $k$ and $S$ are constants. As long as the wavelength is measured, $Z$ can be obtained; that is, the type of element can be determined. The X-ray intensity Ii and the mass percentage concentration Ci of the analytical element satisfy if the element is the same as the experimental condition:

$$I_i = \frac{KC_i}{\mu_m}(i = 1, 2, 3, \wedge) \tag{2}$$

K is a constant, which is related to the incident ray intensity I and the mass absorption coefficient of the analytical element to the incident ray. Besides, m is the total mass absorption coefficient of the sample to X-ray and X-ray fluorescence. Under certain conditions (such as uniform composition of samples and no mutual excitation between elements), there is a linear relationship between Ii and Ci. As a consequence, the corresponding element content can be calculated from X-ray intensity. Because of the simple sample preparation, convenient operation, many measurable elements, fast analysis speed, high precision and no damage to the tested objects, XRF analysis technology is becoming more and more popular in scientific and archaeological work, which is often used to determine the composition of cultural relics, identify authenticity and dating, and so on. The time–space framework is the basis of archaeology. Dating provides a timescale for cultural relics, while the origin of cultural relics and mineral sources provides spatial coordinates. The composition of cultural relics has a certain relationship with the time and place of production. XRF technology to determine the composition of cultural relics and the establishment of a database for cluster analysis, combined with other circumstantial evidence, can deduce the origin and mineral sources of cultural relics and provide a valuable basis for further textual research of the social history at that time.

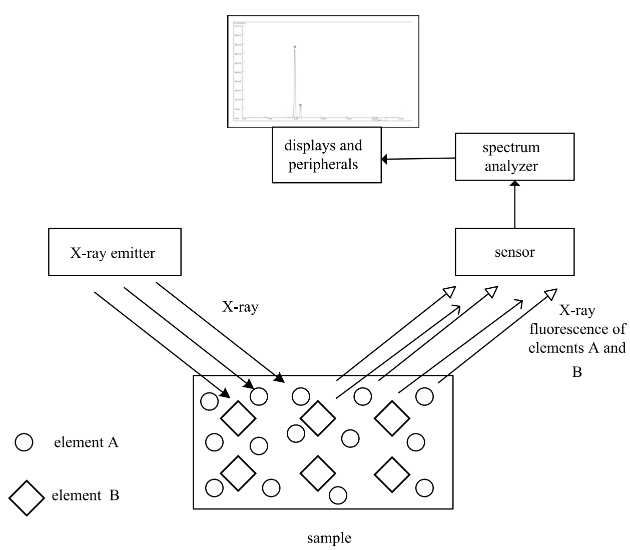


**Fig. 3** The diagram of X-ray fluorescence analysis

## Experimental results

Some bronzes of Shang and Zhou dynasties (Hunan collection) are detected and analyzed by using the above two methods. Moreover, a bronze chime with three sheep patterns of the Shang Dynasty (Figs. 4, 5, 6, 7, No. 1) and a bronze chime (Figs. 8, 9, No. 2) are taken as examples to explain the embodiment of the above methods in the textual research of ancient artifacts, and the test results are used to assist the textual research of the analytical objects. The No. 1 bronze cymbal with three sheep patterns is proved to be a late Shang artifact and should be a cooker. The whole instrument is 22.8 cm high, 14.7 cm in caliber and 1.12 kg in weight and double ears, neck, crotch, three bags of feet,

**Fig. 4** The front view of No. 1

**Fig. 5** The front view of No. 2

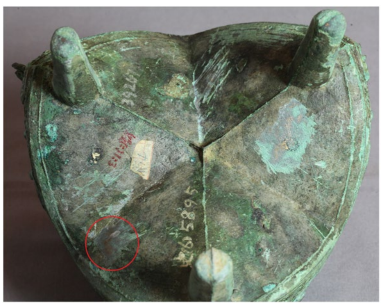

**Fig. 6** The sampling diagram of No. 1

**Fig. 7** The sampling diagram of No. 1

**Fig. 8** The sampling diagram of No. 2

**Fig. 9** The sampling diagram of No. 2

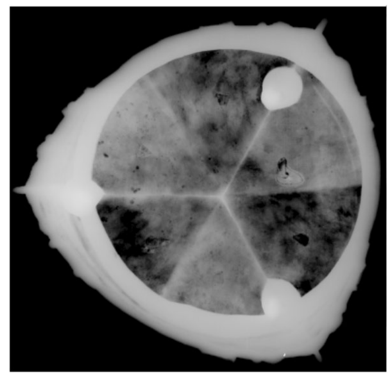

**Fig. 10** The diagram of X-ray fluoroscopy of No. 1

feet nearly columnar [4]. The No. 2 bronze chime is a musical instrument, which is pig-shaped, with a curled upper lip, a bristled mane and a short tail, about 52.5 cm long and 28.8 cm high. The computer X-ray transmission imaging system equipment and the portable X-ray fluorescence spectrum analyzer are used, respectively, and the two are sampled as shown in Figs. 6, 7, 8 and 9.

### X-ray perspective imaging analysis of objects

See Figs. 10, 11, 12 and 13

### X-ray fluorescence Spectral Analysis of utensils

See Tables 1 and 2, Figs. 14 and 15

## Result analysis

It can be seen that the three feet of device 1 are shown in white from the X-ray films of Figs. 10 and 11. Combined with physical observation, there is no hollow in the corresponding position of the three feet in the inner bottom of the abdomen, and there are no signs of core support on the feet, so it is inferred that the feet should be solid rather than

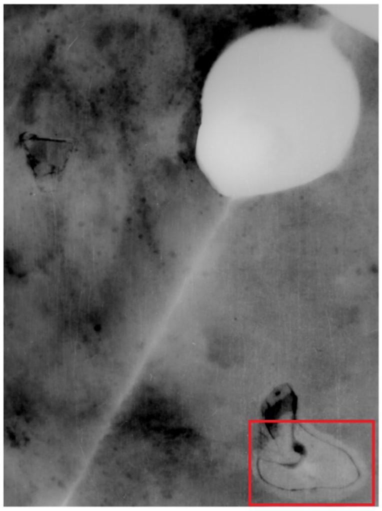

**Fig. 11** The diagram of X-ray fluoroscopy of No. 1

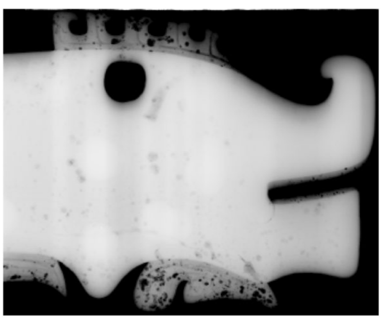

**Fig. 12** The diagram of X-ray fluoroscopy of No. 2' s forebody

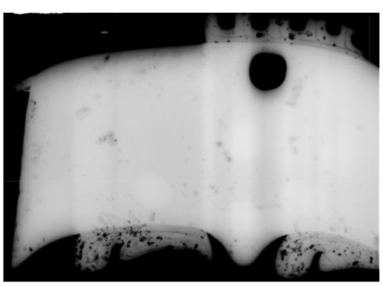

**Fig. 13** The diagram of X-ray fluoroscopy of No. 2's afterbody

**Table 1** The reference table of element content in No. 1

| Main elements | Copper | Tin | Lead |
|---|---|---|---|
| Content (%) | 73.83 | 18.70 | 7.11 |
| Error ± 2σ(%) | 1.03 | 0.22 | 0.11 |

**Table 2** The reference table of element content in No. 2

| Main elements | Copper | Tin | Lead | Iron |
|---|---|---|---|---|
| Content (%) | 87.07 | 7.69 | 1.37 | 2.37 |
| Error ± 2σ(%) | 0.74 | 0.11 | 0.07 | 0.07 |

hollow. There are six white lines in the bottom of the abdomen as the model lines and six points, and the objects are determined to be cast by the model method of clay blocks. There are large pieces of rust or even holes in the ventral floor (a large black area), which are repaired by plaster, epoxy resin and other materials, but are not visible to the naked eye. There is a gasket near the center of each of the six fan-shaped areas, which is nearly triangular, square and so on, which is irregular, and the six gaskets are roughly in a concentric circle and do not drift, so it can be seen that the thickness of the medium-sized cavity is precisely controlled in the casting process; there is a clear boundary between the gasket and the surrounding matrix, indicating that it does not melt with the pouring liquid in the casting process. There are recasting marks near one of the gaskets (the box part of Fig. 11), and the boundary of the patch is obvious. Careful observation also shows a small bright spot on the wall (lower right corner of Fig. 10), where there is suspected to be a high content of lead because of its high absorption to X-rays (impermeable). On the abdominal bottom of another object, there are many black dots and bubble-like areas, which are actually subcutaneous pores or casting shrinkage holes. Similarly, combined with the X-ray films of Figs. 12 and 13, we can see that the No. 2 artifact is relatively well preserved, only the head, the front spine, the title edge and the tail are missing and repaired in the later stage, and the white protruding decoration and part of the ornamentation can be seen. It can be seen that there are a large number of black round or irregular spots on the bristle-shaped mane and front and back feet, and there are also many spots of different sizes on the head and body. These are stomata (visible pores and subcutaneous pores) or shrinkage holes produced in the casting process of utensils. Compared with the No. 1 object, the casting quality of the No. 2 object, especially the mane and foot, is poor. A crack in the lower jaw is also clearly visible after being magnified by the X-ray film.

## Conclusion and discussion

Almost every area of science has been revolutionized by our ability to collect two-dimensional images of increasingly fine detail, ranging from radio signals of far-off solar systems, to high-resolution electron microscopy images by X-ray nanotomography. It can be seen that the metal composition of utensil 1 is mainly copper, tin and lead, which

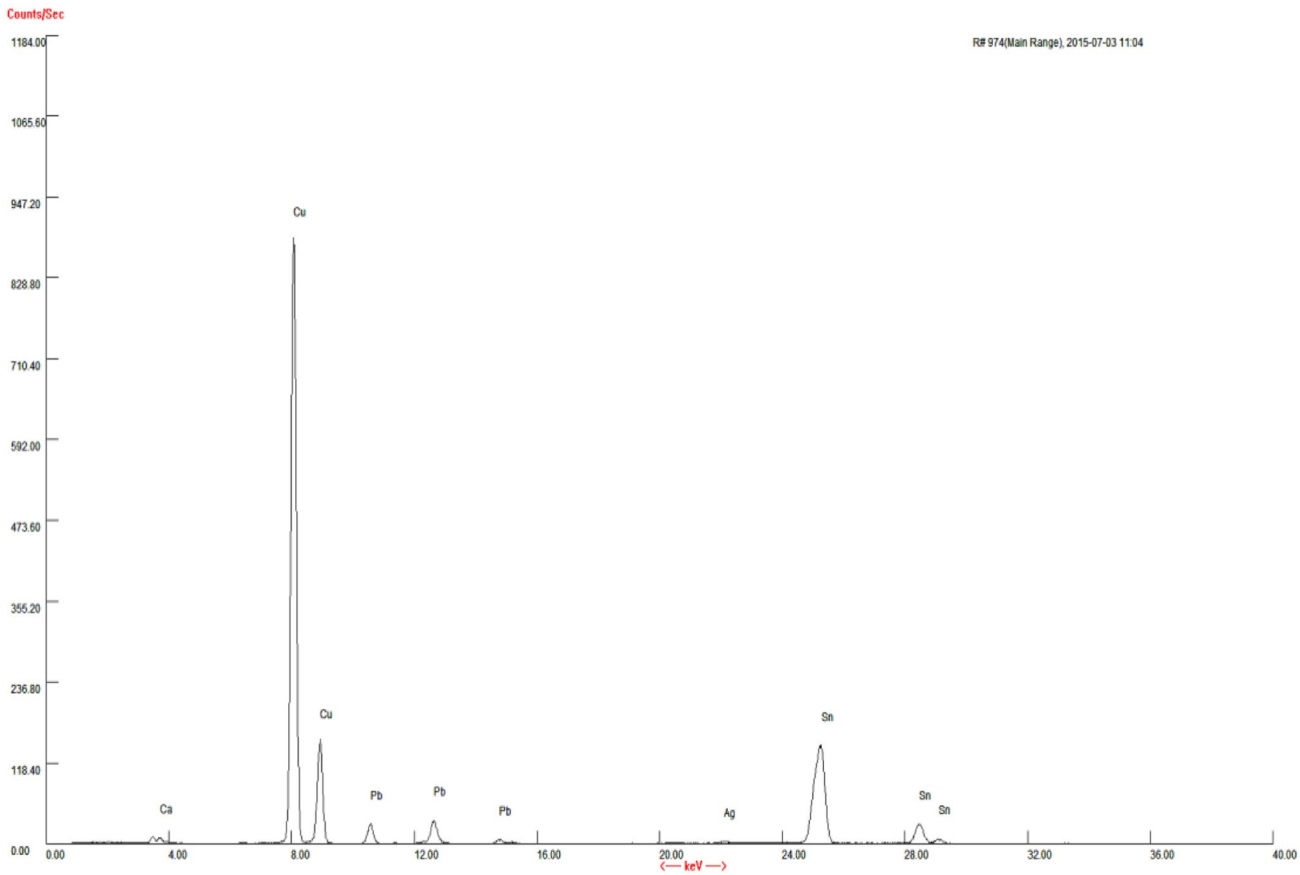


**Fig. 14** The spectrogram of No. 1's X-ray fluorescence

is a typical ancient copper–tin–lead ternary bronze alloy with very small amounts of calcium and silver. It may be caused by impurities, sample contamination, detection errors and so on from the test results of Figs. 14, 15 and Tables 1 and 2. Utensil 2 also belongs to copper–tin–lead ternary bronze alloy objects, but compared with utensil 1, the contents of tin and lead are relatively low, while utensil 1 is rich in tin, reaching nearly 20%, the content of lead is also high, and the content of copper is reduced to less than 80%. Tin can reduce the residual oxygen content in the bronze casting solution and improve its flow properties; especially when the tin content is more than 6–7%, an eutectoid will be formed in the as-cast structure, thus significantly improving the strength, hardness, corrosion and wear resistance [5]. The melting point of the alloy can be reduced by adding tin at the same time, so that the temperature condition of casting can be reached more easily. With regard to the role of lead in bronze alloys, David A. Scott [6] believes that lead can reduce the melting point of the alloy. He Tangkun [7], Qin Ying [8] and other scholars believe that lead can improve the fluidity, formability, machinability and reduce the cost of the alloy. In fact, there is no solid solution relationship between lead and copper or copper–tin alloy in copper–tin–lead ternary alloy, and intermetallic compounds cannot be formed, but can only be dispersed in free or separated state, so as to improve the solidification properties and hinder the coarse crystal structure to improve the casting properties. Compared with object 2, object 1 has a higher content of lead, which is more conducive to casting exquisite objects with fewer defects and delicate and complex patterns. In addition, it is worth noting that there is a high content of iron in artifacts 2, and iron was also detected in many objects tested this time, while China first used iron in the Shang Dynasty and produced iron smelting in the late Western Zhou Dynasty [9]. As a consequence, iron may not be added artificially, but iron was mixed as an impurity and was closely related to bronze casting at that time. Combined with X-ray fluoroscopy and fluorescence spectrum technology, it is more determined that this batch of utensils is cast by mud block casting method, and the gaskets and mud core bracing techniques are widely used, and the contents of tin and lead are generally higher than those in the Central Plains. There is no clear correlation between objects, and the same form of copper–tin–lead ternary bronze alloy and high alloy copper is likely to come from

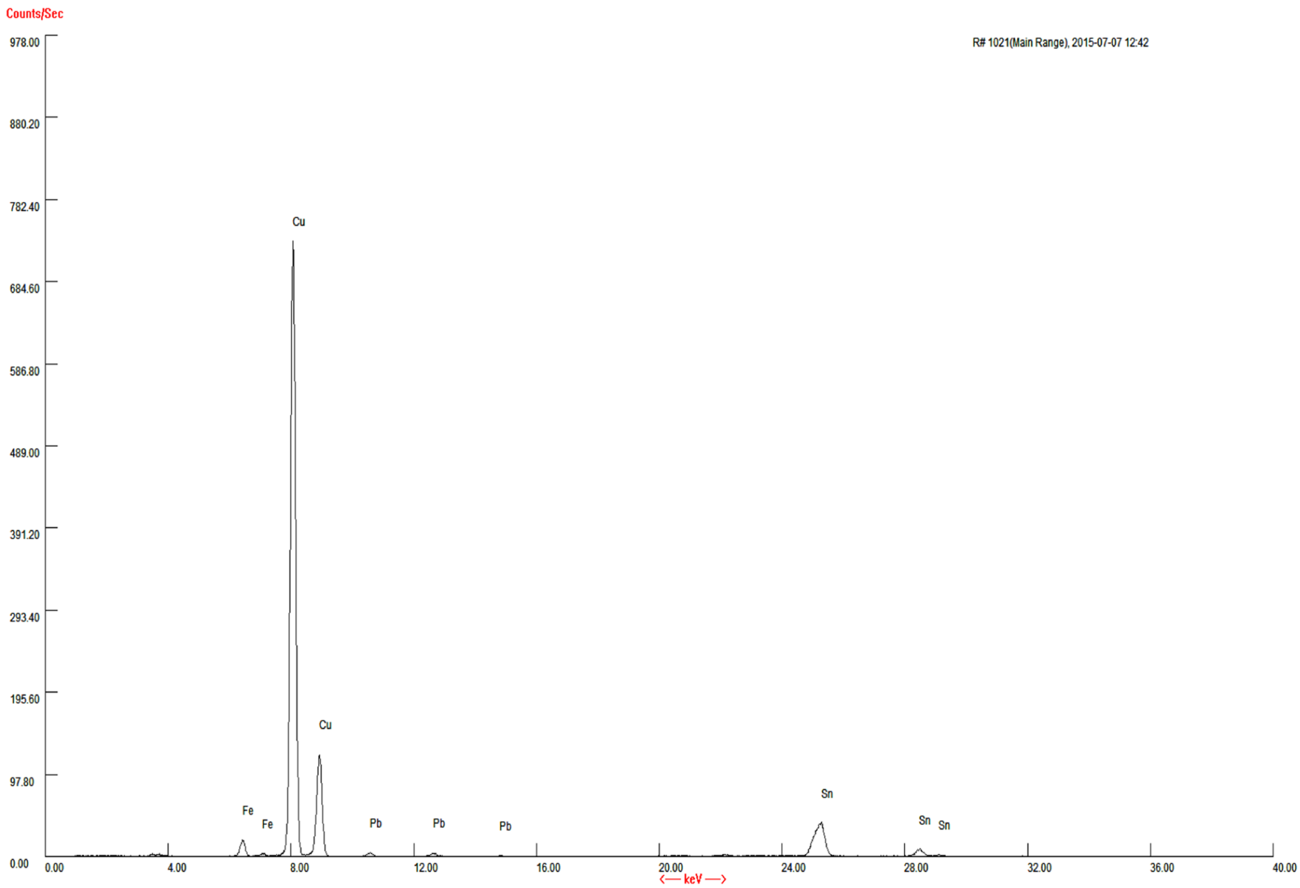


**Fig. 15** The spectrogram of No. 1's X-ray fluorescence

the alloy system with the nature of the times. The Shang and Zhou Dynasties are the key period for the formation and development of the system [10]. The tendency of detection and analysis in this paper support this conclusion. It can be seen that during this period, craftsmen have mastered the methods and laws of the use of copper, tin and lead alloys summed up a set of scientific bronze alloy system [11, 12] and knew how to use different alloy ratios on utensils with different functions, as far as possible to achieve the most beneficial factors such as device manufacturing, performance and economy.

**Funding** This article is a periodical result of the project which called research of bronzes in ba-yu area, and the number of the project is R2019FFY21.

## Declarations

**Conflict of interest** The author(s) declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

## References

1. Mei JJ, Hirao Y, Natsumoto J, et al. (2005) Research on the ratio of lead isotopes in the early bronzes excavated in eastern regions of Xinjiang. Oriental Archaeol (2):303–311
2. Zhengyao J, Chase WT, Hirao Y, et al. (1994) Research on the ratio of lead isotopes in bronzes excavated in the tomb of Shang dynasty located in Dayangzhou town, Xingan county, Jiangxi province. Archaeology (8):744–747+735
3. Xiaohong W, Sixun Y (2000) The pretreatment of bone samples in high-precision 14C dating. Essays of Archaeometry (Volume II). Hefei:Press of University of Science and Technology of China (2):82–85
4. Li W (2011) Culture dictionary of Hunan (2). Hunan People's Publishing House, Changsha, p 586
5. Bocao L (2002) Casting non-ferrous alloys. 2nd ed. Handbook of casting (Volume III). Beijing: China Machine Press p 335
6. Scott DA, Ying J (1995) Selective translation. Microstructure of ancient metals. Sci Conserv Archaeol 7(1):56–60
7. Tangkun H (1997) Synthetic study on the alloying technique for bronze in the pre-Qin period. Stud Hist Nat Sci 16(3):273–286
8. Ying Q, Guofeng W, Wenqi L et al (2005) Experiments on dissolving lead from bronze wares and the related questions. Sci Conserv Archaeol 17(2):16–18

9. Jueming H (1999) Ancient Chinese metal technology—civilization created by copper and iron. Elephant press, Zhengzhou, p 5
10. Rongyu Su, Jueming H, Kemin Li et al (1995) Ancient Chinese metal technology. Shandong Science and Technology Press, Jinan, pp 185–307
11. Turo FD (2020) Limits and perspectives of archaeometric analysis of archaeological metals: a focus on the electrochemistry for studying ancient bronze coins. J Cult Herit 43:271–281. https://doi.org/10.1016/j.culher.2019.10.006
12. Rademakers FW, Farci C (2018) Reconstructing bronze production technology from ancient crucible slag: experimental perspectives on tin oxide identification. J Archaeol Sci Rep 18:343–355. https://doi.org/10.1016/j.jasrep.2018.01.020