Atomic Spectroscopy

Review

Archaeometallomics as a Tool for Studying Ancient Ceramics

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ABSTRACT: In this paper, the concept of archaeometallomics is put forward to study the role of metal elements in cultural relics. An example is the influence of metal elements in the identification of their origin, dating, authenticity and the technology used for the production of ancient ceramics. This analysis also provides the social and cultural connotations of the development process of that time and shows that there is a close relationship between the rich glaze varieties and the metal elements in porcelain. The application of different analytical techniques in studying metallic elements in ancient ceramics is also briefly summarized. The construction of a metal element composition database and the related questions in the glaze color-forming mechanism of ancient relics should be considered an important research direction for future works.

INTRODUCTION

For obtaining archaeological research data，relics from ancient human activities are the materials that help to condense and reflect on the developmental process of ancient history. China is an ancient civilization with a long history and rich in relics such as ancient paintings, stone tools, wooden and jade wares, bronzes, ceramics, etc. Using scientific techniques to extract the information contained in cultural relics has enhanced the research in archaeology and achieved valuable results. Because of the rarity of the samples, various means of nondestructive analysis are widely used to obtain the respective physical and chemical information.

Metallomics is a research field that can provide a systematic understanding of the metal uptake, source of origin, role, and excretion in biological systems.[1,2] Although metallomics was originally focused on the essential roles of metal and metalloids in biological systems, the concept of metallomics has been extended to the study of metals and metalloids in material sciences, such as matermetallomics.[3]

In this study, we propose the concept of archaeometallomics as a tool to systematically study the role of trace elements in cultural relics and clarify the role and function of the metal elements. Archaeometallomics can facilitate the understanding of the origin, the processing technology used, and to verify the authenticity or falsification of cultural relics such as for ancient paintings, ancient stone tools, ancient jade wares, ancient bronzes, and ancient ceramics, etc. In this paper, as an example, we will showcase the application of archaeometallomics in studying ancient ceramics.

Ancient ceramics are among the most outstanding and important historical and cultural heritage of the Chinese nation. They are not only the special carrier of human society and culture but also the crystallization of science and technology of ancient craftsmen. The developmental process used in ancient ceramics contains very rich scientific technology and social and cultural connotations. Tracing the origin, identifying the authenticity or falsification, understanding the development and evolution of porcelain technology are important topics.[4-6] Ancient ceramics are made of clay, porcelain clay, and mineral raw materials and encompass multiple processing procedures. The main components of a ceramic are bodies, glazes, and colors containing elements such as Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, *etc.*, but there are other trace components that also determine the source, the reflection process, etc.

The proportions of metal elements in the raw materials of the body, the glaze and the color of the ancient ceramics are different, which is determined by the geological conditions of the raw materials. They carry the characteristic information of local origin and age, so the study of the content of metal elements in the body, glaze and color of the vessel, can provide important reference information for source and age dating. In the process of high-temperature firing and because of the inherent law of metal elements at different temperatures and different firing atmospheres, rich and colorful glazes are produced. By researching the structure of a metal's color elements, the ceramic firing technology can be deduced, which provides a scientific basis for the restoration of the original in the traditional manufacturing technology. For example, Mn, Fe, Cu, and Co in the glaze at different temperatures and different firing atmospheres contribute to the colorful glaze of ancient Chinese ceramics. The distribution of metal elements and their adjacent atomic structures are closely related to the provenance, dating, and processing technology.[7] It was found that green glaze and red glaze contained Cu as the coloring agent; celadon, white and black porcelain used Fe as the coloring agent, while blue and white porcelain used Co as the coloring agent, *etc.*[8-10] However, the same coloring element in the ceramic glaze color can show different colors and depends on the relationship with the content of the ceramic formula and the firing process.[11] Thus, the composition of the metal element content in the body and glaze of ancient ceramics provides important reference information for provenance and dating identification. Furthermore, the valence state of the metal atoms and the structure can play an important role in establishing the firing technology.

ANALYTICAL TECHNIQUES IN ARCHAEOMETALLOMICS

Due to the particularity of cultural relics like ancient ceramics, nondestructive analysis techniques or micro-damage analysis are always desired. Neutron activation analysis (NAA), X-ray fluorescence analysis (XRF), X-ray absorption fine structure spectroscopy (XAFS), Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), Laser-induced Breakdown Spectroscopy (LIBS) and Atomic Absorption Spectroscopy (AAS) are often used to analyze the content, valence, and structure of metallic elements in ancient ceramics.[12-14] The earliest application of the neutron activation method to ceramic archaeology was in 1954, when Sayre and Dodson at Brookhaven Laboratory of Princeton University, USA,[15] first studied the origin of ancient ceramics. For more than half a century, experts at home and abroad have used neutron activation analysis to carry out a large number of studies on the origin, age and production process of ancient ceramics.[16,17] Neutron activation has gradually become a widely accepted method for trace element analysis in Chinese ceramic archaeology.

XRF was first used in the 1950s to study cultural relics.[18] It has been used more and more widely in the study of ancient ceramics and plays an irreplaceable role.[19-21] With the development of synchrotron radiation source in the 1970s, XAFS has gradually become a practical method of structural analysis on ancient ceramics and can provide the internal physical and chemical information.[22]

NAA. NAA uses neutrons, charged particles and high-energy photons with certain energy to bombard the sample. Radioactive nuclides are generated, which can be used for the quantitative analysis of elements in the sample.[23] Compared with other elemental analysis methods, it has many advantages: first, high sensitivity, high accuracy and precision; second, multi-element analysis, which can give the contents of dozens of elements, especially trace elements; third, the sample size is small, not easy to stain and not affected by reagent blank. The disadvantage is that this method cannot detect elements that cannot be activated by neutrons, nor can the elements with short half-life be measured.

XRF. According to the different excitation sources, the X-ray fluorescence analysis technology is available as X-ray fluorescence (using X-ray tube as the excitation source), synchrotron radiation X-ray fluorescence (SRXRF), and proton-induced X-ray fluorescence (PIXE), etc.[24] As a non-destructive analysis techniques, XRF has been widely used and plays an important role in the study of ancient ceramics.[25,26] The sample is bombarded with photons, electrons, protons, particles, or other ions at a certain energy in which the inner shell (K, L, or M shell) electrons are excited, causing electron transitions in the shell and emitting characteristic X-rays (or auger electrons) of the element. By determining the wavelength (or energy) of characteristic X-rays, it can determine the elements in the sample. The percentage content of an element in the sample can be obtained by measuring the intensity of the characteristic X-ray and adopting the appropriate method for calibration and correction.[27]

XAS. When X-rays pass through an object, they are absorbed by the object and their intensity is changed. This strength decay obeys exponential law. On the high energy side near the absorption limit, the absorption curve presents a fine structure of up and down fluctuations. By measuring, analyzing and calculating this fine structure, much information can be obtained about the arrangement of atoms around the absorption atoms.[28] XAFS is usually divided into two parts: Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Side Structure (XANES).[29] The characteristics of the EXAFS spectrum reflect the near-range coordination conditions around the absorption atoms, while the XANES spectrum is basically compared with the standard reference, and the valence state and coordination environment are qualitatively determined according to the deviation of the absorption edge position, the height and position of the edge front peak. As a non-destructive structural analysis method, XAFS is very suitable for studying the content and state of the coloring elements in ancient ceramics.[30-32]

LA-ICP-MS. LA-ICP-MS is a powerful analytical technology that enables highly sensitive elemental and direct isotopic analysis

Fig. 1 Binary diagrams, using normalized data, of (a) CaO vs MgO and (b) V vs Cr for the amphora samples analyzed. An indication of the kiln site for each individual is given.[36]

of solid samples.[33] The principle of LA-ICP-MS is to focus the laser beam on the surface of the sample to melt and vaporize it. The carrier gas (He or Ar) will send the sample particles (aerosols) to the plasma for ionization, and then mass filtration through the mass spectrometry system. Finally, the receiver will be used to detect ions with different mass charge ratios. In recent years, the micro-elemental and isotope ratio analysis technology of LA-ICP-MS has been further developed and is widely used in geology, metallurgy, environment, biology, chemistry, materials, archaeology and other fields.

LIBS. In LIBS, a high-energy laser is applied to the sample to form a laser spot on the surface of the sample, which causes the sample to excite and glow. The light is then analyzed by the spectral and the monitoring systems, and the elemental composition and the content of the sample are obtained. In recent years, great progress has been made in the theory and application of laser-induced breakdown spectroscopy, especially in the fields of materials, soil, biology, environment, metallurgy, medicine, ancient art and painted cultural relics.[34]

AAS. AAS is based on a sample of measured elemental vapor phase ground state atoms by narrowband characteristic of the atoms of the radiation of the light source to produce resonance absorption. Its absorbance within a certain range and the vapor phase is proportional to the measured element of the ground state of atomic concentration. So, the element content in the sample is measured.[35] AAS has been widely used in various fields, such as geology, metallurgy, machinery, chemical industry, agriculture, food, light industry, biological medicine, environmental protection, material science and so on.

ARCHAEOMETALLOMICS IN THE STUDY OF ANCIENT CERAMICS

Archaeometallomics in studying the origin and dating of ancient ceramics. Ancient ceramics were generally made with local materials, so their production and raw material of origin are the same. In the same region, the clay used to make the body and glaze for the ceramic has certain trace metallic elements in common, and these trace elements are different from other regions, referred to as "fingerprint elements." Fingerprint elements in clay do not change when they are made and fired, and the fingerprint information is retained in the ceramic. The composition and content of chemical elements in ancient ceramics are used to find the common points and differences, and then the origin of ancient ceramics can be identified. Fantuzzi *et al.*[36] analyzed Late Roman amphorae from four kiln sites located in the Guadalquivir River basin (Spain) by using a combination of instrumental analytical techniques, including thin-section optical microscopy, X-ray diffraction (XRD) and XRF. The contents of some metallic elements (Ca, Al, V, Cr, etc.) established the origin characteristics (Fig. 1). The results not only contribute to new evidence on the study of oil amphora production in this region, but also serves as a basis for the identification and sourcing of these amphorae and, consequently, for a better understanding of the trade networks during the Late Roman period.

Prinsloo *et al.*[37] re-dated the Chinese celadon shards excavated on Mapungubwe Hill, a 13th century Iron Age site in South Africa, using Raman spectroscopy, XRF, and XRD. According to the ratio of alkaline earth metals to alkali metals, the date of the Chinese celadon shards was possibly the period of the Yuan (1279–1368 AD) or even the early Ming (1368–1644 AD) dynasty (Fig.2). These results have an impact on the chronology of the history of the region and therefore calls for further research of a comparative nature for other Chinese celadon shards excavated at archaeological sites in Africa, in addition to additional carbon dating of the Mapungubwe hill area.

Fig. 2 Comparison of the CaO:K_2O ratio of Chinese celadon glazes from the Five Dynasties to the Ming Dynasty.[37]

The folk celadon and the Kuan celadon from the Ru kiln were analyzed by Zhang *et al.*[38] using PIXE. The metal elements (Al, K, Ca, Ti, Mn, Fe) and Si found in the glaze were used to differentiate between the Ru Kuan celadons and Ru folk celadons.

Energy Dispersive X-ray Fluorescence (EDXRF) was used by Ma *et al.*[39] to analyze the characteristics of the different kilns used for the production of Tang Sancai wares. Some metal elements became the fingerprint elements of different Tang Sancai kiln sites (Fig.3). The fingerprint elements provide valuable scientific criteria for provenance identification for Tang Sancai pottery of unknown origin.

Blagoev et al. [40] analyzed excavated ceramic fragments to obtain their chemical composition by using ns-LIBS and XRF. Combining different methods and comparing the obtained results, it provided complementary information regarding white-clay ceramic production and the complete chemical characterization of the examined artefacts.

The lead and strontium isotopic composition in pottery is an important feature for identifying the origin of ancient pottery, in addition to the analysis of the main and trace elemental content of the body and the glaze. Zhang *et al.*[41,42] used MS to analyze the lead isotopic composition of ancient pottery samples from the neolithic sites of Jiahu and Xishan in the Henan province. Their study showed that the lead isotopic composition can be used to identify the origin of some ancient pottery samples. The Pb isotopic composition of the ancient pottery from Xishan and Hualing was found similar to the Liangzhu culture, but the Sr isotopic composition was significantly different. Strontium isotope analysis significantly enhances the ability of using isotope composition to identify the origin of ancient pottery.

Fig. 3 Distribution of TiO_2, MnO, and ZnO for Tang Sancai bodied specimens from Huangbu Kiln and Xing Kiln.[39]

It can be seen from the works of the above researchers that the metal element content plays an important role in the origin and date of ancient ceramics. Due to further development of the fluorescence analysis technology, especially the development of energy dispersive X-ray fluorescence analysis (ED-XRF), the analysis range of metal elements in ancient ceramics has been further expanded, the detection limit further reduced, and the accuracy of nondestructive analysis significantly improved.[43] However, in the quantitative process, a series of standard samples close to the matrix of the unknown sample should be used to establish calibration curves.[44] Therefore, it is necessary to prepare standard samples of ancient ceramics, establish calibration curves for a series of standard samples close to the ancient ceramic matrix, and carry out quantitative analysis of unknown ancient ceramics.

Scientific researchers have carried out the development of an ancient ceramic test standard. The Shanghai Institute of Ceramics[45] started the related research in 1999, using geological reference materials as raw materials, and a set of 13 sintered reference materials was preliminary designed and prepared. According to the requirements of solid chemical composition standard samples and the actual need for nondestructive quantitative analysis of ancient ceramics, the Institute of High Energy Physics (IHEP)[46,47] developed a set of standard samples for nondestructive quantitative analysis of ancient ceramics by collecting traditional ceramic raw materials and referring to the content data of principal components in ancient porcelain body of famous kilns. At present, Chinese researchers have accumulated much data on metallic elements in the body and glaze of ancient ceramics, and some institutions have also established specimen databases for comparative analysis. Based on the existing ancient

Fig. 4 (A) Detail of samples SCP4 showing an example of the analyzed areas: (g) glaze, (b) blue and (db) dark blue; (B) Bar chart with the ratio of Fe/Co and Mn/Co oxides for blue (b) and dark blue (db) area.[48]

Fig. 5 Cu K-edge XANES spectra of the samples CLT1 (—●—) and CLT5 (—o—). CuO (cupric oxide) (- - -) and Cu2O (cuprous oxide) (· · ·) compounds, used as standards, are also reported.[53]

ceramic composition database, various statistical methods, such as cluster analysis and principal component analysis, can be used to trace the origin and identify the authenticity of samples from unknown sources.

Archaeometallomics in studying the color mechanism and firing technology of ancient ceramics. Archaeometallomics also plays an important role in the study of the coloring materials used for painted porcelain. Coutinho *et al.*[48] used ED-XRF to analyze the elemental composition of blue and white porcelain fragments unearthed in a monastery in Portugal but from the late Ming Dynasty, and found that the element (Mn, Fe, Co) content ratio of the blue and dark blue regions in blue and white porcelain was different. In the dark blue region, the ratio of Mn/Co is higher and the ratio of Fe/Co is lower. It suggested that ancient potters probably used both Co pigments as shown in Fig. 4(A) and (B). The Chinese underglaze-red porcelain made in the Yuan Dynasty was studied by Cheng *et al.*[49] using the PIXE facility of a 3 MeV tandem accelerator. The results showed that copper was an underglaze-red pigment from the red-colored area on the glazed surface. The obtained CuO content in the red glaze lies in the range 0.2%~6.0%, varying with the degree of red color. The red, yellow, and green colors in three enamel samples were analyzed by Zhao *et al.*[50] The results showed that the main coloring element of red enamel is Au, the yellow enamel contains Pb and Sn, and the green enamel is mainly colored with Cu.

XAFS is suitable for the study of the fine structure of metal elements in ancient ceramic-colored materials and the state of colored metal elements, to discuss the color mechanism and firing technology. XAFS research was carried out by Matsunaga *et al.*[51] on a pottery billet in Turkey where the clay of the vessel was from the vicinity of the dig site. It was found that the absorption edge energy of the Fe element spectrum increased gradually with the color of the unearthed pottery changing from gray to brown to orange. Gray pottery is mainly fired in a reductive atmosphere or a weak oxidizing atmosphere, while yellow pottery is fired in an oxidizing atmosphere.

By using the confocal micro X-ray absorption fine structure (Micro-XAFS) experiments at BL15U in the Shanghai Synchrotron Radiation Facility (SSRF), Zi *et al.*[52] qualitatively analyzed the painting samples of the Palace Museum. It was found that the chemical information of Fe in the painting materials at different depths is similar to that of the natural red soil standard samples. Barilaro *et al.*[53] collected a series of painted pottery fragments excavated in Sicily, Italy, which were identified as products of different historical periods based on the morphological samples, ranging from the 18th century BC to the 16th century AD. Through comprehensive analysis of the K-edge near the edge and extended edge structure of Cu in the sample, and comparison with the fine structure spectrum of CuO and Cu_2O in the standard sample, it was confirmed that the composition of the green pigment in the painted pottery is CuO (Fig. 5).

The coloring mechanism of blue and white porcelain in Jingdezhen was studied by Zhu *et al.*[54] using the X-ray absorption spectrum. Analysis of Mn and Fe in the ceramic glaze and pigment showed that the Mn K-edge X-ray absorption near-edge structure is almost the same, while the Fe K-edge X-ray absorption near-edge structure is different. The results show that the oxidation state of Fe has a clear correlation with the change in pigment color. The origin of the red color glazes decorated on the ancient Jun porcelain has been attributed to the presence of copper clusters and copper oxide or copper oxide alone. Tian *et al.*[8] studied Jun porcelain with a red glaze from the Yuan Dynasty with XAFS. It was found that there was 37% monovalent copper and 63% zero-valent copper in the red glaze layer, and the zero-valent copper mainly exists in the form of metal clusters or polymers. On the surface of the red glaze, it is mainly monovalent copper. The monovalent copper is isolated in the vitreous mesh structure. These special forms of copper lead to the unique optical properties of the Jun glaze.

CONCLUSIONS

In this review paper, archaeometallomics is proposed as a tool to systematically study the role of trace elements in cultural relics, which can facilitate the understanding of the origin, the technology used, and the authenticity or falsification of cultural relics. The application of archaeometallomics for ancient ceramics was showcased as an example. With the continuous development and improvement of various analytical techniques, there are a variety of analytical techniques available today to comprehensively study the metal elements in the body, glaze, and color of ancient ceramics as well as their origin.

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Notes

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REFERENCES

1. H. Haraguchi, *J. Anal. At. Spectrom.*, 2004, **19**, 5-14. https://doi.org/10.1039/B308213J
2. Y. F. Li, H. Z. Sun, C. Y. Chen, and Z. F. Chai, Metallomics. Beijing, Science Press, 2016
3. Q. Li, Z. Cai, Y. Fang, and Z. Wang, *Atom. Spectrosc.*, 2021, **42**, XX-XX. https://doi.org/10.46770/AS.2021.101
4. S. L. Feng, Q. Xu, X. Q. Feng, Y. Lei, L. Cheng, and Y. Q. Wang, *Nuclear Physics Review*, 2005, **22**, 131-134. https://doi.org/10.1111/j.1745-7254.2005.00175.x
5. M. J. Feliu, M. C. Edreira, and J.Martín, *Anal. Chim. Acta*, 2004, **502**, 241-250. https://doi.org/10.1016/j.aca.2003.10.023
6. B. P. Li, J. X. Zhao, K. D. Collerson, and A. Greig, *Chinese Sci. Bull.*, 2003, **48**, 1219–1224. https://doi.org/10.1360/02wb0121
7. Y. B. Yu, M. L. Zhang, J. Wu, Q. J. Li, J. M. Wu, N. Wan, and X. J. Liu, *Jiangsu Ceramics*. 2011, **44**, 12-14. https://doi.org/CNKI:SUN:JSTC.0.2011-01-007
8. S. B. Tian, Y. Z. Liu, M. L. Zhang, L. H. Wang, Y. N. Xie, and C. S. Wang, *Nuclear Techniques*, 2009, **32**, 413-418. https://doi.org/10.1016/S1874-8651(10)60079-8
9. M. Matsunaga and I. Nakai, *Archaeometry*, 2004, **46**, 103–114. https://doi.org/10.1111/j.1475-4754.2004.00146.x
10. L. H. Wang and C. S. Wang, *J. Anal. At. Spectrom.*, 2011, **26**, 1796-1801. https://doi.org/10.1039/C0JA00240B
11. I. Tanaka, T. Mizoguchi, and T. Yamamoto, *J. Am. Ceram. Soc.*, 2005, **88**, 2013–2029. https://doi.org/10.1111/j.1551-2916.2005.00547.x
12. G. Buzanich, P. Wobrauschek, C. Streli, A. Markowicz, D. Wegrzynek, E. Chinea-Cano, and S. Bamford, *Spectrochim. Acta B*, 2007, **62**, 1252-1256. https://doi.org/10.1016/j.sab.2007.08.003
13. Z. M. Duan，J. Liu，Q. L. Jiang，Q. L. Pan，R. W. Li, and L. Cheng, *Spectrosc. Spect. Anal.*, 2019, **39**, 303-309. https://doi.org/10.3964/j.issn.1000-0593(2019)01-0303-07
14. S. H. Zhou, L. Fu, and B. L. Leung, *Spectrosc. Spect. Anal.*, 2008, **28**, 1181-1185. https://doi.org/10.3964/j.issn.1000-0593.2008.05.052
15. E. V. Sayre and R. W. Dodson, *Am. J. Archaeol.*, 1957, **61**, 35-41. https://doi.org/10.2307/501078
16. A. Hein, H. Mommsen, and J. Maran, *J. Archaeol. Sci.*, 1999, **26**, 1053-1058. https://doi.org/10.1006/jasc.1999.0423
17. Y. Lei, *Palace Museum Journal*, 2007, **131**, 86-127,158. https://doi.org/ 10.16319/j.cnki.0452-7402.2007.03.006
18. J. Zhu, Z. W. Mao, and S. D. Zhang, *Spectrosc. Spect. Anal.*, 2006, **26**, 2341-2345. https://www.cnki.com.cn/Article/CJFDTOTAL-GUAN200612047.htm
19. S. L. Feng, X. Q. Feng, J. H. Zhu, G.X. Xie, L. T. Yan, L. Li, G. Li, and Q. H. Shen. *Chinese Phys. C*, 2008, **32**, Suppl.II, 284-288. https://www.zhangqiaokeyan.com/academic-conference-foreign_chinese-physics-c_thesis/020511423906.html
20. L. Li, S. L. Feng, X. Q. Feng, Q. Xu, L. T. Yan, B. Ma, and L. Liu, *Nucl. Instrum. Meth. B*, 2012, **292**, 25-29. https://doi.org/10.1016/j.nimb.2012.09.034
21. L. T. Yan, S. L. Feng, L. Li, B. Ma, L. Liu, and X. Q. Feng, *Archaeometry*, 2015, **57**, 822–836. https://doi.org/10.1111/arcm.12136
22. L. D. Ma, *Shanghai Measurement and Testing*, 2007, **34**, 2-11. https://doi.org/10.3969/j.issn.1673-2235.2007.06.001
23. Z. F. Chai, Basis of activation analysis, Beijing, Atomic Energy Press, 1982.
24. G. Z. Ma, and H. Y. Yao. *Spectrosc. Spect. Anal.*, 1985, 5, 140. https://www.cnki.com.cn/Article/CJFDTotal-GUAN198506140.htm

    Spectrosc. Spect. Anal., 2010, **30**, 3143-3148. https://doi.org/10.3964/j.issn.1000-0593(2010)11-3143-06
25. D. J. Li, Z. Y. Jiang, Y. Sha, Y. Y. Huang, and H. R. Shao,

Archaelogy, 1999, **11**, 86-89,104. https://www.cnki.com.cn/Article/CJFDTotal-GUAN198506140.htm

26. J. K. Guo, H. S. Cheng, X. Q. Chen, R. F. Huang, and X. X. Guo, *Chinese Ceramics*, 1999, **35**, 1-4. https://doi.org/10.16521/j.cnki.issn.1001-9642.1999.03.001
27. A. Ji, G. Y. Tao, S. J. Zhuo, and L. Q. Luo, X-ray fluorescence spectrum analysis, Beijing, Science Press, 2003.
28. Q. W. Wang and W. H. Liu, X-ray absorption fine structure and Its application, Beijing, Science Press, 1994.
29. D. C. Koningsberger, B. L. Mojet, G. E. van Dorssen, and D. E. Ramaker, *Top. Catal.*, 2000, **10**, 143–155. https://doi.org/10.1023/A:1019105310221
30. M. O. Figueiredo, T. P. Silva, and J. P. Veiga, J. Electron Spectrosc., 2012, **185**, 97-102. https://doi.org/10.1016/j.elspec.2012.02.007
31. S. Y. Lee, D. Nathanson, and R. Giordano, *J. Oral Rehabil.*, 2001, **28**, 457-462. https://doi.org/10.1046/j.1365-2842.2001.00717.x
32. L. H. Wang, J. Zhu, Y. Yan, Y. N. Xie, and C. S. Wang, *J. Raman Spectrosc.*. 2009, **40**, 998-1003. https://doi.org/10.1002/jrs.2218
33. A. L. Gray, *Analyst*, 1985, **110**, 551-556. https://doi.org/10.1039/AN9851000551
34. J. Z. Chen, J. Wang, G. J. Ju, X. Li, Y. Wang, and F. Teng, *Chin. Sci. Bull.*, 2016, **61**, 1086-1098. https://doi.org/10.1360/N972015-00439
35. W. Y. Xu, X. R. Li, and B. Guo, *Gansu Agricultural Science and Technology*, 2015, **11**, 76-78. https://doi.org/10.3969/j.issn.1001-1463.2015.11.027
36. L. Fantuzzi and M. C. Ontiveros, *Archaeol. Anthrop. Sci.*, 2019, **11**, 6785-6802. https://doi.org/10.1007/s12520-019-00937-x
37. L. C. Prinsloo, N. Wood, M. Loubser, S. M. C. Verryn, and S. Tiley, *J. Raman Spectrosc.*, 2005, **36**, 806–816. https://doi.org/10.1002/jrs.1367
38. B. Zhang, H. S. Cheng, W. J. Zhao, Z. Y. Gao, G. X. Li, J. Z. Xie, M. Guo, and F. J. Yang, *X-Ray Spectrom.*, 2006, **35**, 27-32. https://doi.org/10.1002/xrs.810
39. B. Ma, L. Liu, S. L. Feng, Q. Xu, and X. Q. Feng, *Nucl. Instrum. Meth. A*, 2014, **319**, 95-99. https://doi.org/10.1016/j.nimb.2013.11.011
40. K. Blagoev, M. Grozeva, G. Malcheva, and S. Neykova. *Spectrochim. Acta B*, 2013, **79-80**, 39–43. https://doi.org/10.1016/j.sab.2012.11.003
41. X. Zhang, L. Ma, J. F. Chen, Z. F. Zhang, P. Qiu, and C. S. Wang, *Nulear Techniques*, 2003, **26**, 693-696. https://doi.org/10.3321/j.issn:0253-3219.2003.09.011
42. X. Zhang, J. F. Chen, L. Ma, J. F. He, C. S. Wang, and P. Qiu, *Nulear Techniques*, 2004, **27**, 201-206. https://doi.org/10.3321/j.issn:0253-3219.2004.03.011
43. F. He and P. J. V. Espen, *Anal. Chem.*, 1991, **63**, 2237-2244. https://doi.org/10.1021/ac00020a009
44. R. Sitko. *Spectrochim. Acta B*, 2009, **64**, 1161–1172. https://doi.org/10.1016/j.sab.2009.09.005
45. J. Wu, Science and technology research and appraisal of ancient ceramics. Beijing, Science Press. 2009.
46. L. Li, S. L. Feng, J. H. Zhu, X. Q. Feng, G. X. Xie, and L. T. Yan, *Nuclear Techniques*, 2010, **33**, 165-169. https://www.cnki.com.cn/Article/CJFDTOTAL-HJSU201003003.htm
47. J. H. Zhu, S. L. Feng, F. Y. Chu, X. Q. Feng, G. X. Xie, L. T. Yan, and L. Li. *Spectrosc. Spect. Anal.*, 2010, **30**, 3143-3148. https://doi.org/10.3964/j.issn.1000-0593(2010)11-3143-06
48. M. L. Coutinho, V. S. F. Muralha, J. Mirao, and J. P. Veiga. *Appl. Phys. A*, 2014, **114**, 695-703. https://doi.org/10.1007/s00339-013-8147-8
49. H. S. Cheng, Z. Q. Zhang, E. K. Lin, and Y. P. Huang, *X-rays for Archaelolgy, pp* 151-158. https://doi.org/10.1007/1-4020-3581-0_8
50. L. Zhao, H. Li, D. Mou，J. H. Wang, and J. M. Miao. International Symposium on Ancient Ceramics (ISAC'09), 2009, 424-433.
51. M. Matsunaga, and I. Nakai. *Archaeometry*, 2004, **46**, 103-114. https://doi.org/10.1111/j.1475-4754.2004.00146.x
52. M. Zi, X. J. Wei, H. S. Yu, Y. Lei, Y. and Y. Huang, *Nuclear Techniques*, 2015, **38**, 060101. https://doi.org/10.11889/j.0253-3219.2015.hjs.38.060101
53. D. Barilaro, V. Crupi, D. Majolino, and V. Venuti. *J. Appl. Phys.*, 2007, **101**, 064909. https://doi.org/10.1063/1.2537908
54. J. Zhu, W. G. Luo, D. L. Chen, W. Xu, C. F. Ming, C. S. Wang, and L. H. Wang, *J. Phys. Conf. Ser.*, 2013, **430**, 012066. https://doi.org/10.1088/1742-6596/430/1/012066