Application of confocal 3D-MXRF technology to the 3D elemental analysis and surface topography imaging of samples

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Abstract. X-ray fluorescence analysis technology (XRF) is widely used in many fields. In this experiment, a three-dimensional confocal microbeam X-ray fluorescence analysis (3D-MXRF) spectrometer built by the laboratory is used to perform deep scanning on single element sample, surface coated sample, and ceramic sample, etc., the new spectrometer has deeper probing depth and better ability to resolve adjacent elements in the sample. The distribution of three-dimensional elements of samples is analyzed and explained. And the surface topography imaging of two samples is performed, and the newly constructed confocal 3D-MXRF was found to have a higher microscopic resolution, which plays a potential role in the popularization of surface inspection and 3D element analysis of industrial products.

1. Introduction
The X-ray fluorescence analysis technology has the unique advantage of non-destructive testing [1]. In particular, the three-dimensional confocal microbeam X-ray fluorescence analysis (3D-MXRF) has smaller focal spots due to the use of microbeam X-rays, which enables 3D surface topography imaging and 3D elemental analysis of samples. Li et al. measured the stratification of metal ions in rock samples, which laid the foundation for understanding the natural growth process of ore and for discriminating rock structure [2]. Nakano and Tsuji conducted a deep analysis of the local lacquerware and obtained a two-dimensional image of a specific layer of the lacquerware [3]. Zhao et al. performed three-dimensional imaging of the micron-scale morphology of the sample surface for the first time on a confocal 3D-XRF spectrometer [4]. A high-power X-ray source with a high-precision translation stage is used in this experiment. Compared with the original spectrometer, the spatial and depth resolution of the new 3D-MXRF has been improved. The 3D elemental analysis of different samples is performed via this spectrometer and combined with the current material manufacturing process, reasonable explanations of the composition of the ingredients are given. The feasibility of 3D-XRF analysis technology for surface topography imaging was verified by experiments on samples with obvious surface undulations.

2. Experimental
2.1. Test instruments
Figures 1(a) and (b) show the new spectrometer and its lens, respectively. The spectrometer mainly consists of five parts marked in figure 1(a) as follows: A represents X-ray tube, B - converging lens, C - sample holder, D - semi-lens, E - semiconductor detector, and F - CCD camera.

![Spectrometer Diagram](image)

**Figure 1.** (a) Three-dimensional confocal X-ray fluorescence spectrometer (b). Images of lenses.

The source is a Mo target x-ray micro-focus source (Oxford Instruments Ultra Bright 9600 series). A poly-capillary lens-focusing system was developed by our laboratory. The lens system parameters: A full lens (total length=40 mm, entrance focal length=48 mm, exit focal length=16.4 mm) is assembled with the X-ray source, and a half-lens (total length=12.3 mm, entrance focal length=10.9 mm) is configured with the detector.

The sample holder (SURUGASEIKIDS112) is an X-Y-Z 3D translation stage controlled by the computer; the resolutions of the X-, Y-, and Z-axes are 4, 2, and 2 μm per pulse, respectively.

A CCD camera is employed for sample positioning.

The detector: An x-ray silicon drift detector (Amptek X-123) is used to obtain the fluorescence spectrum; the detector’s energy resolution is 145 eV at 5.9 keV.

A schematic of the 3DXRF spectrometer is shown in figure 2. Under the condition of a voltage of 30 kV/15 W, the confocal voxel is calibrated by a Ni-Cr wire with a diameter of 25 μm, and a confocal analysis voxel with a size of 46.27μm×52.35μm×52.52μm is formed by the two-lens confocal structure [5]. Compared with the confocal analysis voxel of the original confocal spectrometer, which is 56.7μm×64.1μm×53μm, the X, Y, and Z axial spatial resolution of the new spectrometer is improved, which shows that the new lens performs better than those of the original spectrometer. The confocal voxel is fixed, and the translation stage moves the sample in the X–Y–Z directions, which is equivalent to the confocal voxel moving inside the sample [6]. Under the condition of a voltage of 20 kV/1 mA, single-element samples (iron and nickel sheets), coated samples (iron fund film, iron-based nickel film), and a multi-element ceramic sample (ceramic vial) were subjected to depth scanning using the
spectrometer. The detecting depth was about 250μm, elements within 10μm and above from the sample could be clearly distinguished.

Figure 2. Schematic diagram of the 3DXRF spectrometer based on poly-capillaries.

2.2. Results and Discussion
2.2.1 Application of 3D-MXRF in elemental analysis of sample. (1) Imitation blue-and-white porcelain of the PRC. The tested sample is a fragment of the blue-and-white porcelain bowl of the PRC, as shown in figure 3.

Figure 3. A fragment of the blue-and-white porcelain bowl and the analyzed area.

In the experiment, since the surface of the ceramic sheet is relatively smooth, the analysis is performed when the confocal voxel is just inserted into the surface of the sample, the detector has the highest count rate at this time. The experimental conditions: the voltage and the current are shown in Table 1, the scanning steps of the X and Y axes are both 160μm, a total of 17 (X-axis) * 19 (Y-axis) = 323 points are scanned, the scanning area is 2.72mm (X-axis) * 3.04mm (Y-axis). The scanning time for each point is 100s.

Table 1. The voltage and current conditions for all experiments in this paper.

| Voltage(kV) | Current(mA) |
|------------|-------------|
| 20         | 1           |

The blue-and-white porcelain glaze was made of unrefined cobalt ore in the early Ming Dynasty. It has a high content of Mn and Co. The porcelain has more green and blue tones after the medium term
because it was made of refined cobalt ore, which has a lower content of Mn. The blue and white color of the sample is dim; it can be seen that it is made of unrefined cobalt. It can be observed in figure 4 that it has a high content of Mn. The intensity distribution of the Co indicates that the cobalt material was used as a raw material for drawing blue and white at the early stage. The Fe element is not only distributed in the cobalt material, but also in the kaolin for firing the carcass, so the distribution of the iron element is found to be irregular in the figures. Both the innermost carcass and the outermost enamel contain calcium, the enamel is thin in the blue and white, so the Ca is mainly distributed around the blue and white.

![Figure 4. Distribution of elements. (a) Co; (b). Mn; (c). Fe; (d) Ca.](image)

(2) The green leaf pattern on the ceramic vial.
The experimental material is a green leaf pattern on the ceramic vial, as shown in figure 5.

![Figure 5. Glazed colored ceramic vial and the analysis area.](image)

The test conditions involved the voltage of 20kV and current of 1mA, Scanning steps of X- and Y-axes were both 40μm. A total of 33 (X-axis) * 13 (Y-axis) = 429 points were scanned, the scanning area
was 1.3mm (X-axis) x 0.4mm (Y-axis). The scanning time for each point is 100s. The green leaf tip on the sample surface in figure 5 was scanned. The distribution of each element is shown in figure 6.

The distribution of the elements clearly shows the shape of the tip. As can be seen in figure 6, the Fe, Co, Cr, and V elements measured in the carcass are distributed around the tip. These elements are mainly derived from kaolin, which is used to make carcasses. The distribution of Cu and As elements in the tip portion is obvious, indicating that the green pigment of the tip is mainly derived from patina, which is formed during the firing process that divalent copper ions are fused to the glaze.

Three-dimensional elemental analysis was performed on two representative samples, and the distribution and content of different elements were given, the elemental distribution is fully compatible with the morphology of the analysis area. The chemical composition of the elements is determined by the combination of the production process and the color of the pattern. The new spectrometer with a high-power X-ray source has a higher fluorescence count rate and reduced the analysis time significantly. The use of a high-resolution monolithic capillary lens set reduces the focal spot size and greatly improves the resolution of adjacent elements in the sample.

![Figure 6. Distribution of elements. (a) As; (b) Fe; (c). Cr; (d) Co; (e) Cu; (f) V.](image)

2.2.2 Application of 3D-MXRF to the surface topography imaging of samples. (1) The word "Guo" on the positive side of a dime coin of the PRC.

As shown in figure 7, a dime coin with a prominent surface is selected, and the word "Guo" is placed on the sample stage (The word “Guo” is written in Chinese: “国”, it means “country”). The experimental conditions: the voltage is 20kV, and the current is 1mA, the scanning steps of the X-axis is 100μm, scanning distance is 2mm, the scanning steps of the Y is 100μm, scanning distance is 2.5mm, a total of 20 (X-axis) * 25 (Y-axis) = 500 points are scanned. The entire scan time is about 4h. The number of pulses on the surface depth of each point is obtained, and a three-dimensional figure is drawn, as shown in figure 8.

The color bar on the right side represents the depth in the form of pulses, each pulse representing 2μm. It can be calculated that the surface height of the word "Guo" is about (140-105)* 2 =70μm. It can also be seen from the left side that the upper and lower concave depths of the word “Guo” are almost the same, and the fluctuations are small. The word is at the millimeter level, and the confocal spot diameter is about 50 μm, which indicates that the surface topography of the sample with the undulation of more than ten micrometers can be basically measured. And the scanning image of the word “Guo” is
clear, indicating that it is feasible to obtain the surface topography of the sample by 3D-MXRF analysis technology.

(2) The word "E" on the opposite side of a dime coin of the PRC.

As shown in figure 9, the word "E" is placed on the sample stage. The experimental conditions: the voltage is 20kV, and the current is 1mA, the scanning steps of the X-axis is 40μm, scanning distance is 1.12mm, the scanning steps of the Y is 40μm, scanning distance is 1.2 mm, and the total of 28 (X-axis) * 31 (Y-axis) = 868 points are scanned. The entire scan time is about 6h. The three-dimensional figure is drawn, as shown in figure 10.

It can be calculated that the surface height of the word "E" is about (1810-1790) *2=40μm. On the left side of the word “E”, near the letter R area, the depth of depression is small, on the right side of the word “E”, near the letter N, the depth of depression is larger. The height difference between the two sides is about (1820-1810) *2=20μm. It can be seen from the right side of the image that the surface of the word "E" has a large surface undulation.

Three-dimensional scanning imaging experiments were performed on the surface of the coin; the imaging results of the experiments completely fit the surface topography of the samples, which shows the microscopic features of the analysis area. Good fitting results are obtained for the undulation around the surface pattern of the coin, which confirms the feasibility of the 3D-MXRF analysis technology in the surface topography imaging of samples.

3. Conclusion
In this study, the spectrometer was improved in structure and performance. Elemental analysis of ceramic samples using the new spectrometer revealed the composition and content distribution of elements that fully reflect the ceramic surface pattern. The chemical composition of the carcass, enamel, and glaze was analyzed. Scanning and imaging the surface of the words “Guo” and "E" of a dime coin yielded the results that were highly consistent with the real image. The experimental results show that
the confocal 3D-MXRF analysis technology has a high utility value in three-dimensional elemental analysis and topography imaging of samples.

Acknowledgment
This study was financially supported by the National Natural Science Foundation of China (NSFC) (11675019, 11875087).

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