Study of confocal 3D micro X-ray fluorescence analysis technique based on polycapillary X-ray lens

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Abstract. This study realized the microcell analysis using confocal area formed by a pair of polycapillary X-ray lens, built a 3D micro X-ray fluorescence spectrometer, elaborated the controlling software, and analyzed the 3D scan performance of the set-up via its measured and calculated basic parameters. The depth-detecting performance of the developed set-up was assessed by scanning several samples of Cu-Mo thin film on silicon base and red-green porcelain of Ming dynasty under different conditions. In addition, through surface-adaptive scanning, the scanning and identification of the fractures and fine cracks of the ceramic samples revealed the morphology of samples, which was consistent with the theoretical model.

1. Introduction
Since the capillary system can change the direction of X-ray propagation, its application in micro-XRF analysis is much more than just obtaining high-intensity X-ray microbeams. For example, the use of a catheter system in front of the detector allows the detector to receive only the fluorescent X-rays from the specific micro-regions of the sample, thereby enabling micro-analysis of the sample [1-3]. Simultaneous use of the catheter system in front of the X-ray source and the detector, a confocal structure composed of the two can be used to detect a specific micro-region of the space, achieve the depth analysis, as well as to assess a three-dimensional element distribution [4, 5]. Ordinary micro-XRF can only get the two-dimensional element distribution of the sample. “Polycapillary X-ray lens confocal" means that the exit focal spot of the polycapillary X-ray converging lens of the excitation channel and the entrance focal spot of the polycapillary X-ray parallel lens of the detection channel coincide. When the two lens axes are perpendicular and coplanar, the polycapillary X-ray parallel beam lens can only collect X-ray signals from the confocal volume of the focal spot, as shown in figure 1.

The sample moves with a three-axis translation stage, so the foci can reach almost any spot in the sample. According to the set motion range, the X-ray fluorescence intensity spectrum of each micro-element detecting point is obtained in turn, and the fluorescence spectrum of all points in the entire detecting space range is subjected to subsequent processing, and the spatial distribution of chemical elements in the sample can be obtained.
2. Experimental

2.1 Experimental instruments and methods
The 3D-MXRF confocal setup is shown in figure 2. The experiment used the RTW company’s X-ray tube as the X-ray source (MCB5.0 model), with the rated power of 15W, the highest voltage of 50kV, and the maximum current of 1000µA. The detector was controlled by the PX4 X-ray multi-channel analyzer from Amptec. The translation stage consisted of three axes normal to each other (the X-Y axis plane being the horizontal plane, and the Z-axis being normal to the X-Y plane). The minimum step size could be set to 0.625 micrometers. The limiting stroke of each axis was 30 mm. The CCD camera was used to assist in the positioning. The polycapillary focusing and parallel lenses were independently drawn in the laboratory. The former one was mounted in the window of the X-ray source and the latter one on the triaxial inspection frame together with the detector. The polycapillary focusing lens had a length of 62 mm, and its front and back focal distances were 41.9 mm and 17.1 mm, respectively. The polycapillary parallel lens had a length of 20.2 mm, and its focal distance was 10.8 mm.

![Figure 2. The 3D-MXRF confocal setup.](image)

(A) translation stage; (B) CCD; (C) polycapillary focusing lens; (D) X-ray tube; (E) polycapillary parallel lens; (F) semiconductor detector

2.2 Experimental results and data analysis
2.2.1 Scanning of the metal and ceramics. The maximum depth of the sample that can be detected by the 3D-XRF spectrometer directly determines the spatial extent of the three-dimensional analysis. The main purpose of designing a non-destructive 3D X-ray fluorescence spectrometer is to understand the types, contents and distribution of chemical elements inside the sample without destroying the sample. Therefore, the designer always hopes to increase the maximum depth of detection of the spectrometer,
and the depth detection performance becomes an important consideration for the confocal 3D-XRF spectrometer. When the X-ray fluorescence intensity increases from zero to the peak, and then gradually decreases from the peak to zero, the depth range, through which the confocal detection micro-element passes is the maximum detected depth, is defined in this study.

In this paper, samples of different substrates were selected to explore their ability to detect the depth. Experimental method and parameter conditions involved the light source (a Mo target with a maximum power of 10W). The two-lens confocal area of the constructed 3D-XRF spectrometer was used as the detecting micro-element, and the selected points of each sample were scanned in the depth direction at a fixed step size of 10 μm. After the total count of each point was normalized, a "count-deep" relationship curve was constructed, and the depth of detection was obtained at a position where the tail of the curve started to saturate steadily toward zero. Wherein, the starting point of the scan was obtained by fine-tuning the sample platform along the Z-axis, and the position, at which the counting rate started to saturate. That is, the zero point (starting point) of the depth detection was obtained when the confocal spot contacted the surface of the sample. The metal sample was a Cu-Mo thin film on silicon base of the Nanomaterials Laboratory of Beijing Normal University, as shown in figure 3. The thickness of the Cu-Mo film was 530 μm, and the processing parameters were as follows: 229V, 75mA, t=140s for Mo; 390V, 50mA, t=50s for Cu; T=40℃

Test conditions involved the peak voltage of 30kV, current of 150μA, step depth of 10μm, and count time of 5min/point. The obtained count-depth curve is shown in figure 4.

![Figure 3. Partial view of the Cu-Mo thin film on silicon base (photographed by CCD).](image1)

![Figure 4. Normalized count-depth curve of the Cu-Mo thin film on silicon base.](image2)

As can be seen in figure 4, counting started at 50μm and increased as the depth of the spot micro-element entered the sample. The peak was reached at 160 μm. As the depth continued to increase, the count begins to decrease rapidly due to the absorption and scattering of the substrate prevailing. When the depth exceeded 250 μm, the fluorescence intensity has approached zero. According to the above definition, the maximum detected depth was about 200μm (50-250μm).

The porcelain sample which was purchased from the market is a red-green porcelain of the Ming Dynasty. The green glaze and the white porcelain bottom of the sample were respectively detected, as shown in figure 5.

Test conditions involved the peak voltage of 30kV, current of 150μA, step depth of 10μm, and count time of 5min/point. The obtained count-depth curve is shown in figure 6.
The count of green glaze dots was much higher than that of white porcelain, which had to be adjusted by the normalization. The detecting depth of the green glaze spots was about 210 μm, and the white porcelain point was about 240 μm.

2.2.2 Surface adaptive scanning of confocal 3D-MXRF spectrometer. The process of surface adaptation is shown in figure 7. Suppose the confocal micro-element scans the surface of the sample along an axial direction. The solid circle is the end position of the micro-element at each point, and the dashed circle is the temporary position after the axial translation from the current position according to the given step. Its process is roughly as follows:

(1) At the initial position, pre-adjust the micro-element until the count appears, record $Z_1$ or use the initial point 0 as the reference system;

(2) After sweeping the last point, move to the next point along an axial direction according to the pre-set step size:

A. If the point is not counted or the count rate is too low, it is considered to have left the surface of the sample and moved a certain distance in the direction of the sample surface (ignoring the possibility that it may have entered the sample without counting), counting again, evaluating the count rate, Repeat the process until the count rate meets the condition and record $Z_n$;

B. If there is a count and the judgment condition of the count rate is satisfied, it is considered that the micro-element has entered the sample, and the distance should be increased until the count rate is no longer higher than the set value, and record $Z_n$;

(3) Repeat the process in step (2) to finally return the $Z_n(Z_n)$ value for each point in the axial direction. Among them, a small step size of the micro-element moving in the depth direction is 10 μm, and the discriminating time for each point is 5 s. Obviously, when the $Z_n$ value of all points on the surface of the sample is obtained, it is equivalent to obtaining the surface distribution of the sample.

The samples of blue and white tiles are the fragments of the imitation blue-and-white porcelain bowls of the PRC. The tiles have fine cracks and broken glaze areas, as shown in figure 8. The surface scanning is performed on the two positions respectively, and the scanning parameter of the fine crack area A is 30 kV, 300 μA, the scanning point number is 12×15, and the step length is 100 um; The scanning parameter of the break trace area B is 30 kV, 300 μA, the number of scanning points is 10×10, and the step length is 100 μm. The surface topography of the fine crack position A is shown in figure 9, and the surface topography of the broken area B is shown in figure 10.
Figure 7. Schematic diagram of surface adaptive algorithm.

Figure 8. The imitation blue-and-white porcelain bowls of the PRC.
(A) A fine crack (B) Break marks

Figure 9. Surface morphology of area A.

Figure 10. Surface morphology of area B.

The inclination of the surface topography of the sample in the figure indicates that the sample placed on the sample platform is not parallel to the coordinate plane;

The slight depression at the crack and the obvious bending of the surface of the fracture zone of the tile also reflect the surface state of the actual sample. Such a result is not possible without the use of an adaptive surface scanning method but with conventional three-dimensional scanning. For the surface of the sample with a tilted surface and a sharp depression, the conventional three-axis sequential scan will lose fluorescence information at many positions, and the obtained fluorescence intensity information cannot reflect the true element distribution.
3. Conclusions
In this paper, the principle of capillary lens X-ray optical devices and X-ray fluorescence analysis is studied. A three-dimensional microbeam X-ray fluorescence spectrometer with confocal structure formed by integral X-ray lens is built. The depth detection performance of the spectrometer is measured in this study. The surface-adaptive scanning method was developed to eliminate the interference caused by the roughness of the sample surface and the tilt of the placement. After scanning and identifying the sample, the morphology of the sample is well restored, which is consistent with the theoretical model. The results of the surface scan can also be used for three-dimensional distribution scans of elements within the sample.

In the follow-up studies, the authors intend to improve the spectrometer performance, increase the depth of detection, in order to perform a wider range of spatial scans on samples of research value. The results obtained allow one to obtain the spatial distribution of sample elements quickly and accurately, laying the foundation for the wider application of confocal X-ray fluorescence spectrometers.

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