Construction and application of a micro-area polarized energy dispersive X-ray fluorescence spectrometer with polycapillary X-ray lens in a conventional laboratory

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Abstract. The polarized energy dispersive X-ray fluorescence analysis method can effectively reduce detection limits by improving the signal-to-noise ratio. However, the lack of high-power density and small analysis area of the polarized X-ray beam has hindered more accurate analysis of samples in conventional laboratory. A polycapillary X-ray lens can be applied to micro-area analysis. Therefore, a micro-area polarized energy dispersive X-ray fluorescence spectrometer based on a bent highly oriented pyrolytic graphite and a polycapillary X-ray lens is proposed. The polarization degree of the polarized X-ray beam is 99.76% and its focal spot size is 338.8 μm × 404.5 μm. The new spectrometer feasibility was proved by effective production of high-resolution element distribution maps of a holly (Ilex chinensis Sims) leaf sample.

1. Introduction
Energy dispersive X-ray fluorescence analysis (EDXRFA) is a simple and fast technique that enables multi-element analysis of a variety of materials. Considering a triaxial geometry with a second target, the sensitivities and detection limits obtained by EDXRFA in a direct excitation can be significantly improved by using the so-called polarized energy dispersive X-ray fluorescence analysis. Excellent limits of detection of tens of parts-per-million (ppm) are achieved for many elements of interest, which are most valuable in chemistry, biology, environmental science, and geology [1-6]. Hence, manufacturers have recently invested in abundant research and development efforts to provide commercial polarized energy dispersive X-ray fluorescence spectrometers, namely Spectro XLAB 2000 and Epsilon-5. The former has been mainly used to analyze the elements of sunflowers, foliage and spice [7-10], while the latter has been focused on the fluorescence analysis on saline, geological, and environmental indicators and pigments because of its high power [11-14]. However, both of these commercial spectrometers have stringent requirements on the sample dimensions, which diameter should exceed 20 mm. For example, a study reported that the Epsilon-5 irradiated an area of a target sample of approximately 7 cm² [15]. A relatively smaller detection area with the polarized target may cause some problems when analyzing light elements in pressed pellet samples or when the samples are not homogeneous enough [16]. When a geochemical sample was analyzed by a Spectro XLAB 2000, the polyethylene cup-backed pellet was formed with a net specimen diameter of 34 mm [17]. The leaves need to be dried, crushed and turned into a 32 mm diameter pressed powder pellet when analyzed by the spectrometer [8]. In addition, M. Bayazit also said that only 3 samples were big enough to gain the
required quantity of sample powder to use in analysis in an investigation employing a Spectro XLAB 2000 [18]. Therefore, a higher density polarized X-ray beam is needed to irradiate the analytical sample.

Polycapillary X-ray lenses play an important role in the development of X-ray technology, and they have been applied in many fields such as medicine, archaeology, porcelain, foods and chemistry [19-25]. One kind of polycapillary X-ray lens can transform parallel beams into a small focal spot for which the power density gain could be up to $10^4$. Therefore, polycapillary X-ray lenses are widely used in X-ray micro-area analysis [26-28].

In this paper, we present a micro-area polarized energy dispersive X-ray fluorescence spectrometer (micro-PEDXRFS) based on a bent highly oriented pyrolytic graphite (HOPG) and a polycapillary X-ray lens. The bent HOPG was precisely adjusted with a θ-2θ turntable, and a polarized X-ray beam with a polarization degree of 99.76% can be obtained. The polycapillary X-ray lens focused the polarized X-ray beam onto a micron-sized polarized spot. The spatial resolution of the polarized X-ray beam was enhanced by means of the method. The micro-area polarized energy dispersive X-ray fluorescence spectrometer (micro-PEDXRFS) was used to obtain the distribution of elements in an area of a holly (Ilex chinensis Sims) leaf.

2. Experimental

2.1. The generation of a polarized X-ray beam

When the angle between the incident X-rays and the outgoing X-rays is 90°, the outgoing X-rays are linearly polarized. In other words, vibrations parallel to the incident plane no longer travel along the outgoing X-rays. The three-dimensional PEDXRF was designed as shown in figure 1. The X-ray emitted from the X-ray source is non-polarized, and the X-ray after the secondary target is linearly polarized. After irradiating the sample, the original polarized spectrum will not propagate along the direction of the detector. Consequently, for a fluorescence spectrum of the sample, the noise of the original spectrum is reduced.

![Figure 1. The schematic diagram of polarized X-rays production. The red (A) and blue (B) planes are the two-dimensional vibration components of non-polarized X-rays, the yellow line (solid line) is the transmission path of X-rays and the green line (dashed line) is the fluorescence signal.](image)

Figure 2 shows a general view of the experimental measurement setup. The experiment was conducted using an X-ray diffractometer comprised of an X-ray source and θ and 2θ turntables. In figure 2, a is the copper target X-ray source, which has a square focal spot area of 25 mm$^2$ and a maximum
power of 1200 W, and a water-cooled system is needed when it operates. \( b \) is a diaphragm with a diameter of 4.7 mm. \( c \) is a bent HOPG with a radius of curvature of 224 mm and was placed on the \( \theta \) turntable. \( d \) is a sodium-iodide detector placed on the \( 2\theta \) turntable. The sodium-iodide detector has a 254 mm\(^2\) active area. When \( \theta \) and \( 2\theta \) were zero, the X-ray source, the bent HOPG and the sodium-iodide detector were collinear.

To obtain a sufficiently polarized X-ray beam intensity, \( \theta \) and \( 2\theta \) turntables need to be rotated to find the angle with the maximum detector count. To improve the measurement accuracy, a silicon drift detector (SDD, KETEK GmbH AXAS-D50), with an active area of 50 mm\(^2\) and energy resolution of 139 eV, was placed on the \( 2\theta \) turntable, instead the sodium-iodide detector. Then, \( \theta \) and \( 2\theta \) turntables were rotated to find the position where the SDD accurately obtained the maximum count by the control variable method. The measurement results are recorded in table 1. As shown in table 1, we obtained the maximum count and the values of \( \theta \) and \( 2\theta \) corresponding to the maximum count. The maximum count was 6.9×10\(^4\) when \( \theta \) and \( 2\theta \) were 45° and 88°, respectively.

Table 1. The X-ray counts for different \( \theta \) and \( 2\theta \) values.

| \( \theta \) (°) | 49 | 48 | 47 | 46 | 45 | 44 |
|---------------|----|----|----|----|----|----|
| \( 2\theta \) (°) | 96 | 94 | 91 | 89 | 88 | 88 |
| Maximum count | 1430 | 1600 | 2250 | 5600 | 68500 | 30000 |

For the polarized X-ray beam, the degree of polarization \( P \) is defined as in [29]:

\[
P = \frac{1 - \cos^2\alpha}{1 + \cos^2\alpha}
\]

where \( \alpha \) is the angle between the incident and emergent X-ray beams above the bent HOPG plane, which can be written as \( \alpha = 180° - 2\theta \). The \( 2\theta \) corresponding to the maximum count are used to calculate \( \alpha \), the result of which is 92°.

The polarization degree of the polarized X-ray beam is 99.76%. It can be seen that this polarized X-ray beam has a high polarization degree.

2.2. Micro-PEDXRF setup

A polycapillary X-ray lens was used to focus the polarized X-ray beam. The length of the polycapillary X-ray lens is 51.5 mm. The inlet and outlet diameters of the polycapillary X-ray lens are 7.6 and 6.0 mm, respectively. The inlet and outlet diameters of each capillary are 7.06 and 5.90 \( \mu \)m, respectively, in the polycapillary X-ray lens. The output focal length of the polycapillary X-ray lens is 72 mm. A five-dimensional adjusting frame (SURUGA SEIKI) was used to adjust the polycapillary X-ray lens. The focal spot of the polycapillary X-ray lens was measured by the traditional knife-edge scanning method. Figure 3 shows the integral and differential curves at focal spots for this method. The full width at half
maximum (FWHM) of the differential curve is defined as the focal spot size. The spot sizes along the horizontal and vertical directions were 338.8 and 404.5 μm.

![Figure 3](image1)

**Figure 3.** (a) Scanning integral (black) and differential (red) curves of the horizontal position of the focal spot 72 mm from the exit of the polycapillary X-ray lens. (b) Scanning integral (black) and differential (red) curves of the vertical position of the focal spot 72 mm from the exit of the polycapillary X-ray lens.

We scanned the polarized X-ray beam at different positions f from the outlet end of the polycapillary X-ray lens. Table 2 shows the FWHMs for horizontal scanning at different positions.

| f (mm) | 60  | 63  | 66  | 69  | 72  | 75  |
|--------|-----|-----|-----|-----|-----|-----|
| FWHM (μm) | 373.6 | 354.4 | 344.5 | 344.2 | 338.8 | 399.0 |

A holly (*Ilex chinensis* Sims) leaf was placed at the focal spot (72 mm) of the polycapillary X-ray lens. The voltage and current of the X-ray source were 30 kV and 20 mA, respectively. As shown in figure 4, the SDD was used to record the fluorescence signal at positions A and B with a live time of 1000 s. The fluorescence spectra are shown in figure 5.

![Figure 4](image2)

**Figure 4.** The schematic diagram of the experimental setup with two positions of the SDD.

As seen in figure 5, the original spectrum peak for Cu (8.04 keV), in red (solid line), which was detected from position B, is a strong signal. In addition, the strong signal of Cu could disturb other fluorescence signals. However, the signal strength of Cu in the green (dashed line) spectrum measured
at position A is so weak that the Cu Kβ is almost zero, and the signal strength of Ca in the green (dashed line) spectrum is almost the same as that in red (solid line). Therefore, the polycapillary X-ray lens has almost no influence on the polarized X-ray beam. Because of the small focal spot size and the good analysis performance, we named the whole experimental apparatus “micro-PEDXRFS” when the detector was at position A.

Figure 5. The fluorescence spectrum of the holly leaf. The green (dashed line) spectrum is measured at position A, which is polarized. The red (solid line) spectrum is measured at position B, which is non-polarized.

2.3. Analysis by micro-PEDXRFS
A holly (Ilex chinensis Sims) leaf, which was collected on the campus of Beijing Normal University, was scanned by the micro-PEDXRFS with a blue frame area of 5 mm × 4.6 mm, and the spectral collection time was 30 s per time for each measurement. The holly leaf was placed on the sample stage. To prevent overlap of two consecutive measurement areas, the adjustment frame was stepped 0.4 mm and 0.5 mm in the horizontal and vertical directions, respectively. A two-dimensional adjustment frame was used to adjust the sample stage.

Figure 6 shows the element distribution maps of K Kα, Ca Kα, Fe Kα and Cu Kα in the scanning area. The element distribution maps of K and Ca elements show the shape of the leaf and the elemental distributions of K and Ca in the leaf. K and Ca are mostly distributed in the stem of the leaf and less distributed at the leaf edges, which is well consistent with the leaf absorption of trace elements. And at the edge of the leaf K is more abundant than Ca. However, the element distribution map for the Cu element only shows the shape of the leaf and not the elemental distribution in the leaf. The reason is that the detector received a scattering of Cu by the leaf. The scanning of the Fe element also cannot provide the shape of the leaf, because it exists in the experimental environment.

Figure 6. The holly leaf sample, distributions of K, Ca and Fe elements in the scanning area, and Cu scattering by the leaf.
3. Conclusions
To obtain a high power density polarized X-ray beam and improve spectrometer spatial resolution, a micro-PEDXRFS with a polycapillary X-ray lens was set up in the laboratory. The polarization degree of the focusing polarized X-ray beam is 99.76%, with a focal spot size of 338.8 μm × 404.5 μm. The distribution maps of K and Ca elements in a holly leaf are obtained by the micro-PEDXRFS. The micro-PEDXRFS has a wide application prospect in the field of micro-area analysis such as for the accurate detection of small-sized and low-element substances. Some fluorescence analysis experiments in synchrotron radiation can be substituted by micro-PEDXRFS in the laboratory efficiently. Although the copper target X-ray source analyses fewer elements in the holly leaf and the focal spot size of polycapillary X-ray lens is larger, this experiment is the first time that the micro-PEDXRFS has been set up by us, which is very innovative. In the future, we will use a higher power X-ray source and a polycapillary X-ray lens with a smaller focal spot size to improve the micro-PEDXRFS micro-area analysis ability.

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