POLYCAPILLARY OPTICS AND X-RAY ANALYTICAL TECHNIQUES

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ABSTRACT
This paper is a brief review of recent developments in the use of monolithic polycapillary optics in the analysis of materials. Strongly focused X-ray beams can greatly increase the sensitivity and spatial resolution for micro x-ray fluorescence (MXRF) studies. Recent high-resolution measurements with position sensitive diffraction spectrometer (PSDS) detectors have shown that resolution of a few eV can be achieved, making possible measurements of chemical shifts as well as increased sensitivity for composition determinations. The use of polycapillary collimating optics and weakly focusing optics can also give greatly increased sensitivity and convenience in conventional diffraction analysis and for macromolecular crystal structure studies.

I. INTRODUCTION
Research on capillary X-ray optics was started in 1931 by F. Jentzch and E. Nähring (1). A. Rindby [2] and others published the first article in 1986 on the application of tapered monocapillaries for increasing the power density of X-rays in X-ray fluorescence (XRF) experiments. At the same time the polycapillary X-ray focusing system was introduced by M. Kumakhov (3). Later, the rapid progress of capillary optics included design and manufacture of monolithic polycapillary optics (4). A monolithic X-ray collimating or focusing lens is made up of tens, or even hundreds of thousands of capillary channels fused into a single bundle. It is made by drawing a bundle of glass capillaries to the desired shape with a drawing tower. The monolithic lens is compact, solid, with high efficiency and is very convenient for most applications.

At present, three kinds of monolithic X-ray optics are available: focusing optics (for XRF analysis); slightly focusing quasi-parallel beam optics (for single crystal X-ray diffraction (XRD) analysis); and parallel beam collimating optics (for wavelength dispersive XRD analysis). These three types are shown schematically in Fig. 1.

In addition, the remarkable scatter-rejection properties of polycapillary optics can be utilized for monolithic angular filters for mammography and other applications (5).

\textbf{Figure 1. Schematic representation of three types of monolithic polycapillary optics}
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In the present paper, we give a short review of applications of polycapillary monolithic optics for X-ray analysis, and discuss their advantages, limits, and expected further development. There have been a number of articles concerning the study and application of monolithic X-ray optics including some review papers (6-9).

II. MICROBEAM X-RAY FLUORESCENCE (MXRF)

For XRF analysis, monolithic polycapillary optics capture and focus X rays from small-spot divergent X-ray sources or capture and focus parallel X-ray beams from synchrotron radiation sources. The main advantage of X-ray lenses for microanalysis is that they can collect and focus X-rays, forming a very small beam spot (down to 10-15 µm (10), greatly increasing the power density of the X-ray beam (sometimes more than 1000 X). Further reduction of the beam spot size is difficult technologically, since a smaller spot requires a very short output focal distance, inconvenient for X-ray detection.

The main characteristics of a focusing lens are: transmission efficiency, gain, spot size, and output focal distance (8). These parameters are dependent on the energy of the X-ray photons (8,11-12). Actually the efficiency of propagation of X-rays in capillaries by external multiple reflection is dependent on the refractive index and absorption coefficient of the capillary material and on the specific geometry of the optic such as the capillary channel diameter and curvature. As an example, in Fig.2 is shown the dependence of the transmission and focal spot size of lens F1 on the X-ray photon energy (12). Both experimental measurements and theoretical simulations are shown. The lens parameters are: length, 50 mm; entrance diameter, 5.38 mm; exit diameter, 4.36 mm; maximum diameter, 6.8 mm; input focal distance, 67 mm; output focal distance, 13.8 mm. For Mo Kα (17.4 keV) X-rays, the measured values are: focal spot size, 28 µm; transmission, 1.04%; gain of power density, 1629.

![Figure 2.](image)

**Figure 2.** a) Transmission efficiency of lens F1 as a function of X-ray energy, and b) focal spot size of lens F1 as function of X-ray energy

It can be seen that for low energy photons, the transmission efficiency is higher. The high-energy limit of the transmission bandwidth of the lens is determined by the critical angle for total external reflection of X-rays from the wall of the capillary. The lower energy limit is defined by absorption of X-rays in the window of the X-ray tube, air and the capillary wall material. In practice, it is best to make a special design and manufacture in accordance with the particular application.

Monolithic polycapillary focusing optics have found wide application in MXRF analysis in pure and applied scientific research and industry since X-ray spectrometers based on these optics have high sensitivity (with detection limits down to subpicogram) and high spatial resolution (100-10 µm, even 1
At the beginning of this new century the analysis of micromaterials and detailed analysis of extremely small samples by microbeam X-ray fluorescence is increasingly important. "There is an increasing awareness that in order to understand the working of a macrosystem, we require information of microscopical details since most natural and technological systems are intrinsically heterogeneous" (13). As indicated above, we here define MXRF analysis to occupy the dimensions of tens of microns to 1 micron. These are the sizes, for example, of cells, biological macromolecules, aerosol particles, microcrystals, magmatic inclusions within minerals, etc. Therefore the focusing lens can be applied in physics, chemistry, biology, medicine, material science, life science, earth science, environmental science, semiconductor industry, microelectronics and other industries, even in forensic medicine and archaeology.

Recent developments can be found in (14-20). It is of interest to point out that in (20) two focusing lenses were applied to improve the detection sensitivity of MXRF analysis of radioactive materials. The first was used to increase the power density of the X-ray beam incident on the radioactive sample, and the second was placed between the sample and the detector to increase the flux of fluorescent X rays on the detector while at the same time sharply discriminating against background radiation from the radioactive sample. This method could have many uses in nuclear engineering and materials analysis. Another success in (20) was the use of a position sensitive spectrometer that simultaneously gives high spatial and energy resolution and high sensitivity. A schematic representation of such a system is shown in Fig. 3. Fig. 4 and Fig. 5 show X-ray fluorescence spectra measured with this system. The energy resolution achieved depends on the X-ray wavelength as shown in Fig. 6. This is comparable to the energy resolution obtained with scanned wavelength dispersive X-ray fluorescence (WDXRF) systems or microcalorimeter detector based XRF systems, and can be used for chemical as well as compositional analysis.

In (21) a focusing lens was used to increase by 300 X the sensitivity of a superconducting X-ray detector. Such a third generation energy dispersive detector has very high energy resolution (<10 eV), but a very small detection area. An X-ray focusing lens was used to collect divergent X-rays emitted from a sample excited by an intense electron beam in a Scanning Electron Microscope (SEM) and focused the secondary X-rays onto a ~300 µm diameter detector. In this way the effective collection area was >25 mm², comparable to a high-resolution semiconductor detector. This application...
takes advantage of the broad energy bandwidth of polycapillary optics. In environmental studies, a strong focusing lens can be used for single particle XRF analysis of aerosol samples. In such a measurement, one can use an aperture (1-5 µm diameter) to limit the beam size sufficiently to measure a particle separated from other particles. In this case it may be useful to employ a high power rotating anode X-ray generator. On the other hand, single particles can be isolated on a thin organic substrate film and examined with the 20-30 µm focused beam directly from the optic. In many cases, it is sufficient to examine a collection of particles with the focused beam and a compact low power x-ray source can be used.

III. X-RAY DIFFRACTION ANALYSIS

Parallel beam X-ray optics have been extensively used in diffraction studies (8, 9, 22-32). Parallel beam X-ray diffraction is the most important method used for material structure analysis. The parallel beam of previous diffraction instruments is obtained with an aperture with a large loss of X-ray intensity. The use of a collimating lens gives tens or even hundreds of times higher intensity than an aperture, since it can collect X-rays over an angle of several degrees emitted from a divergent X-ray source and convert them to a quasiparallel beam with 0.1-0.2 degrees divergence (depending on the energy) (20).

There are two components in the angular divergence from a monolithic polycapillary optic: the global divergence (or total divergence of the beam envelope), which defines the angular resolution of a diffractometer and the local divergence discussed above which influences the quality of local diffraction patterns. Generally speaking, the angular resolution of the central part of a collimating lens is better than that of the periphery. In principle, the local divergence can be made small if a very small X-ray source spot is used, if the channel size at the lens input is small and well aligned, and if the curvature of the channels is very smooth and free from slope error (also called waviness). At the present time the best angular resolution is about 0.10° for Cu Kα radiation which is worse than the resolution from a conventional diffractometer. But the parallel beam lens can give tens of times stronger X-ray beam intensity, thereby greatly increasing the efficiency for diffraction measurements.

Since the parallel beam lens redirects divergent X-rays into parallel channels, it always increases the
small-angle portion of emitted X-rays. So it can bring large benefit to diffractometers with very fine angular resolution such as double-crystal or four-crystal diffractometers. In this case one can put the lens between the X-ray source and the monochromator to increase the primary X-ray beam intensity. It is worth pointing out that since the lens forms many superfine quasi-parallel X-ray beams, in diffraction experiments, it does not have the focusing circle effect of conventional goniometers. So in the case of parallel-beam geometry the lens tolerates a greater positional error and makes adjustment of the instrument much easier in comparison with the standard Bragg-Brentano geometry. Moreover there are almost no line position changes due to sample displacements, sample roughness or shape or sample transparency in such a parallel-beam geometry compared to the usual parafocusing or Bragg-Brentano geometry.

Fig. 7. X-ray intensity gain of a parallel beam X-ray lens. Setting: Cu tube with point focus X-ray generator, 12 μm Ni filter, 40 kV, 40 mA, 5 mm aperture at lens exit. Fig. 8. Texture pole figures. In the top figure the statistics is improved by 40 x. In the bottom figure, the measurement time is reduced from three days to one hour.

An important step in development of use of the polycapillary optics in diffraction analysis is the design and performance of high-flux X-ray crystallography systems, optimized for diffraction measurements from small macromolecular crystals [25-30]. Earlier applications of polycapillary optics were basically related to improvement and reconstruction of available diffractometers. But M. Gubarev and others combined a small polycapillary collimating optic with only 0.91 mm input diameter, 1.8 mm output diameter and 10.14 mm length and high transmission efficiency of 41% (for the Cu Kα line) and a microfocus X-ray generator (40 W, 40 μm anode spot size). They obtained an X-ray flux of quasi-parallel beam through an aperture of 250 μm diameter which was 16 times higher than that from a 3.15 kW rotating-anode generator equipped with a pyrolytic graphite monochromator [25]. In this case, the input focal distance of the polycapillary collimating optic was only 2.6 mm which required a specially designed microfocus X-ray source which could allow the lens to be very close to the X-ray source spot. Subsequently, even higher (7x) x-ray intensity was obtained and the x-ray intensity and the quality of the diffraction patterns from a protein crystal were comparable with that obtained with 5 kW rotating anode sources equipped with optimally aligned concentric multilayer focusing mirrors (26). This is quite a
new type of diffractometer, which takes full advantage of the: high collection efficiency of polycapillary optics, the small size of the X-ray beam, and the low power, size and flexibility of the X-ray source. Furthermore, a slightly focusing monolithic optic can form X-ray beams less than 0.5 mm in diameter increasing the power density of the beam by another order of magnitude with sufficient parallelism that one can use standard crystallographic software, Such systems should find a wide application in X-ray microanalysis. It is generally accepted that Synchrotron X-ray sources are the best choice for final, high resolution protein structure studies. However, for routine screening of protein and other macromolecular crystals the low power, inexpensive, “table top” polycapillary optic based system can play an important role.

It has also been recently shown that even more strongly focused beam diffraction can be used with even higher intensity and smaller beam spot size. This is analogous to the well known convergent beam electron diffraction. For such convergent beams, the diffraction spots are elongated tangentially about the center of the beam direction (31). For such strongly focused beams the volume of reciprocal space, which is accessed in a single measurement increases compared to parallel beam diffraction and the diffraction spots become streaks. The effects of the one-dimensional streaking for a single-crystal protein diffraction patterns, are in good agreement with theoretical simulation (29) and do not result in untenable overlap for most crystal orientations. Software for analysis of highly convergent beam diffraction has been developed successfully (32).

4. CONCLUSIONS
Polycapillary X-ray optics or so called Kumakhov X-ray lenses were an important breakthrough in X-ray optics in the 1990s, which have made possible the modulation and control of wide bandwidth X-ray beams and have enabled the efficient use of X-ray sources. They have found wide application in X-ray analytical techniques, improved the performance of X-ray analytical instruments, promoted the innovation of some new X-ray instruments and opened up new fields of application.

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