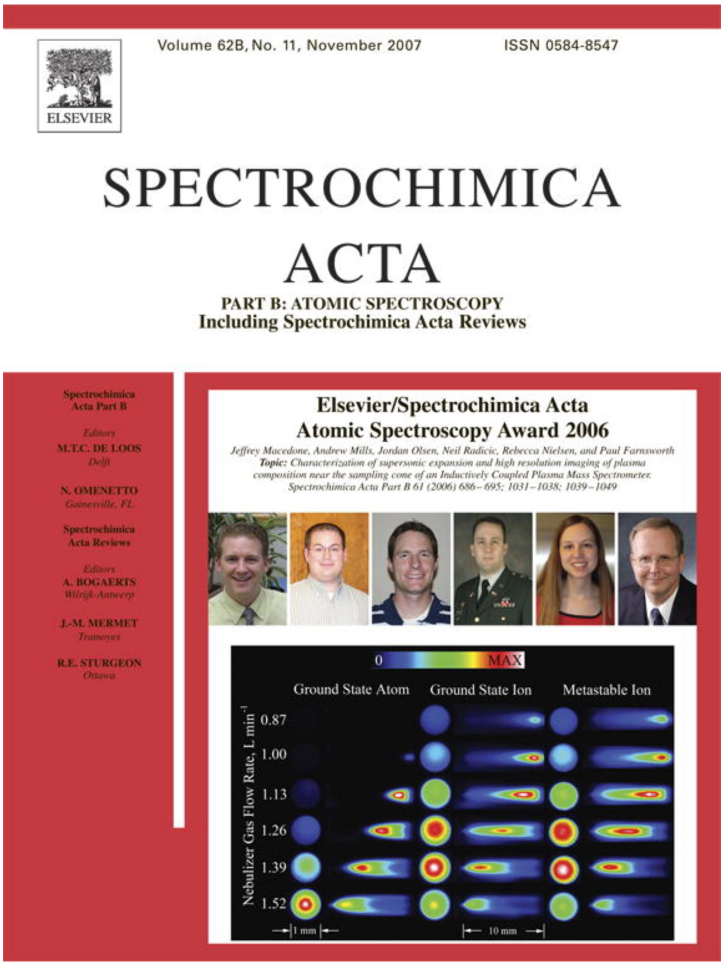
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SPECTROCHIMICA ACTA PART B

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On the use of polycapillary structures to improve laboratory Energy-Dispersive X-ray Diffractometry and Reflectometry ☆

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Abstract

One of the major limits of the laboratory X-ray sources is represented by their low photon flux which induces many researchers to move to synchrotron beamlines. From this point of view, polycapillaries lenses represent an extraordinary tool to improve the performances of laboratory machine and, indeed, several models of polycapillary optics-based instruments, such as diffractometers, spectrometers etc., are currently available on the market. In this work, the application of polycapillary optics to a particular kind of non-commercial X-ray instruments, namely the Energy-Dispersive X-ray Diffractometers and Reflectometers, is proposed. The advantages and limits of the use of polycapillaries are discussed and the results of preliminary experiments are shown.

Keywords: Polycapillary optics; X-ray diffraction; Energy-Dispersive X-ray Diffraction

1. Introduction to polycapillary optics

Manipulating X-rays is one of the major targets of the research in X-ray optics. Devices able to guide and focus X-rays would solve many problems in various branches of science, technology and industry that make use of X-ray techniques, like spectroscopy and diffractometry. Nowadays several methods enabling to manipulate X-ray are known [1]. Nevertheless, they are all based on two phenomena, either refraction, diffraction or reflection of the radiation. In general, in refraction and diffraction conditions, the radiation is strongly absorbed by materials. The absorption can be reduced making use of reflection optics, which work in the total external reflection regime, i.e. at very small angles of incidence. However, in all the cases, the acceptance angles are usually rather small, so that these systems are suitable only for synchrotrons, free electron lasers and other powerful sources characterized by radiation beams having small divergences and small transverse cross-sections. Sources based on the X-ray tube technology, instead, cannot take much advantage by conventional optical devices. From this point of view, polycapillary optics is one of the most promising techniques for solving the problem. The basic idea consists of deflecting X-rays over large angles ϑ, i.e. significantly exceeding the critical angle of total external reflection $\vartheta = \omega_0 / \omega$ (where ω_0 is the plasmon energy of the optics material, ω is the photon energy), by means of multiple reflections inside the capillary channel [2,3]. A polycapillary optics is formed by many bundles of capillaries (thousands or even millions), which guarantee a high acceptance section, tapered in a specific shape. This allows managing X-rays for specific tasks as, for instance, X-ray focusing, formation of quasi parallel beams, etc [4,5]. Presently, polycapillary optics reached the 5th generation, being characterized by submicron channel diameters and working at photon energies higher than 40 keV. The focusing polycapillary lens enable condensing of a $\varnothing = 1$ mm radiation beam in a spot of about $\varnothing = 1$–10 μm and the increase in the radiation flux is significant even for rather low transmission coefficient. For example, at 10% of lens transmittance, the radiation intensity gain may reach 10^3–10^4.

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For diffraction experiments, the most important parameters are the angular divergence of the primary beam and its cross section at the incidence plane. The polycapillary optics capability of converting divergent X-ray beams into quasi-parallel ones, even when their transverse cross section is much larger than that suitable for a conventional slit-based collimation systems, is therefore very interesting.

Due to dependence of total external reflection on critical angle, which is in turn a function of the energy, a given polycapillary optics (with specified geometrical parameters) is expected to work at best in a well defined energy range. As a consequence, a rather good transmittance is typically obtained for the optimal energy, but a certain suppression of the soft part of radiation spectrum is expected. As well, the high energy tail of the radiation spectrum is cut by the transmission outside the channel walls ("cutting-off"), because the critical angle decreases with energy. Fig. 1 presents a typical spectra of a polychromatic X-ray radiation before and behind a polycapillary optics. The aim of the present work is to compare this theoretical prevision with experimental data in order to quantify in more rigorous terms the impact of such effects on the emerging X-ray beam.

2. Outline of the Energy-Dispersive X-ray Diffraction and Reflection

A detailed discussion of the Energy-Dispersive X-ray Diffraction is reported elsewhere [6–8]. Here the basic information for the readers who may not be familiar with this non-standard techniques are given.

By definition, a diffraction pattern is the curve representing the intensity of an X-ray beam diffracted by a sample as function of the magnitude of the momentum $\Delta\mathbf{p}$ transferred from the X-rays to the core electrons of the sample atoms. The magnitude of $\Delta\mathbf{p}$ is generally expressed in h (Planck's constant) units and takes the name of scattering parameter q.

The scattering parameter, in turn, can be expressed as the product of the X-ray energy E and of $\sin\vartheta$, where ϑ is a half of the diffraction angle. Therefore, two ways are available to carry out the q-scan in order to plot the diffraction pattern, namely it is possible either to fix E and to make a ϑ-scan (Angular Dispersive mode) or, reversely, to fix the angle and to scan E (Energy Dispersive mode). The former method is the standard one and all the commercial diffractometers are based on it; the latter can be regarded as a spectrometric way to perform diffraction measurements, since a polychromatic radiation is used as the primary X-ray beam. In this case, the energy spectrum of the primary beam is modulated by diffraction and the resulting diffracted radiation is analysed by a solid state detector performing the energy scan electronically. The q-resolution of EDXD is lower than that of ADXD because, in addition to uncertainty on ϑ, the uncertainty on the determination of E must be taken into account, too. Nevertheless EDXD has some advantages connected to the static geometry of the instrument during data acquisition and due to the higher penetration of the incident radiation, since the energy of the beam is higher (typically up to 60 keV) than in ADXD.

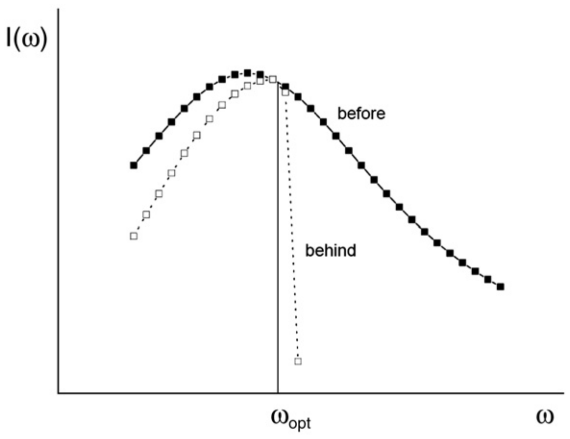

Fig. 1. Expected spectral distributions of X-ray radiation before and behind a polycapillary optical element. An energy cut-off is clearly visible at frequencies higher than the optimal one (ω_{opt}) for which the optics was designed.

The same applies when Reflectometry measurements are to be carried out. Indeed, (far from the ionization thresholds of the sample atoms) also the reflected intensity is a function of the scattering parameter q. In this case, the decrease of q resolution is not a serious problem, since the typical features of the reflection patterns are either long period oscillations (films) or very broad peaks (multilayers and superlattices). On the other hand, the static geometry represents a fundamental advantage because, at the very small angles required to perform a reflectivity measurement, even minimal misplacements or angular uncertainties result in serious relative errors that may compromise the measurement. A schematic draw of the Energy-Dispersive X-ray Diffractometer–Reflectometer is shown in Fig. 2.

3. Advances in polycapillary lenses use for EDXD

As mentioned above, optical devices able to focus X-rays, as refractive glass lenses concentrate visible radiation, already exist [9,10]. Examples are the Fresnel zone plates based on diffraction and the batteries of hollow metal blocks ("parabolic lenses") based on X-ray refraction. However, in the former case, only soft X-rays, much below the range of interest of EDXD applications can be effectively focused; in the latter case, hard X-rays can actually be focused but, due to the small deviation induced by each block of the battery, many blocks must be used and this causes a strong absorption. Furthermore, even when some dozens of blocks are utilized, the focusing lengths are of the order of several meters, i.e. too long for standard laboratory applications.

Finally, both methods are affected by a serious flaw that couldn't be eliminated even if zone plates with extremely narrow grooves or if blocks with an optimal absorption to refraction ratio could be produced. Such flow consists of the unavoidable chromatic aberration effect that would produce an energy-dispersed focal spot, rather than a point-like focus where all the energetic components are overlapped. Other variants of these focusing systems exist, but they all have similar limitations.

For this reasons, techniques based on the use of polychromatic ("white") X-ray beams cannot take advantage of such

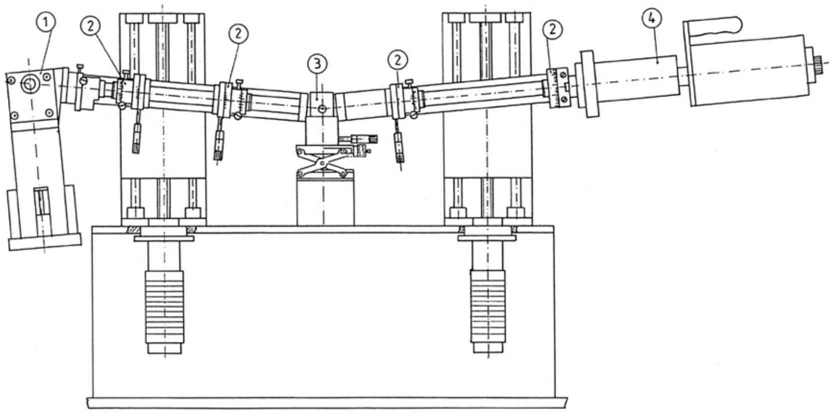

Fig. 2. Sketch of an Energy-Dispersive X-ray Diffractometer/Reflectometer. (1) X-ray tube; (2) collimation slits; (3) sample holder; (4) Ge single crystal solid state detector.

focusing devices for increasing the photon flux by concentrating the beam in a smaller transversal section.

A solution to the aberration problem may be represented by polycapillary lenses, since their working principle is based on the reflection, rather than of the refraction, of X-rays. Indeed, if the incidence angle of a photon (at any energy) on the "air–glass wall" interface of a capillary is below the critical angle (for that energy), it will be mirror-reflected regardless of its energy (neglecting the absorption). Therefore, at least in principle, the various energetic components of a white beam will behave in the very same way and they all will be focused in the same point. Alternatively, if a polycapillary half-lens, which acts as a plane–convex glass lens does with visible radiation, is used, X-rays of any energy will emerge almost parallel to the polycapillary longitudinal axis.

From the practical point of view, it means that, if the spot of an X-ray tube anode is placed in correspondence of the polycapillary half-lens focus, the half-lens will collect all the photons emitted within its acceptance solid angle and transmit the radiation in the form of a polychromatic quasi-parallel beam. Such beam can be used to perform Energy-Dispersive X-ray Diffraction measurements with no need of any collimation slit.

Another advantage with respect to the conventional laboratory collimation slits system is that the sample can be arbitrarily close to the half-lens exit. Indeed, in this case, the parallelism of the X-rays is guaranteed by the polycapillary shape and is not the consequence of the collimating geometry, namely of the high distance between the slits in comparison with their apertures. For this reason, the diffractometer–reflectometer can be designed with a very compact geometry without prejudice of its angular resolution.

For what discussed, polycapillary half-lenses may have the double function of collectors of X-rays emitted in a wide solid angle by the anode spot and of collimation devices, since they select a single direction of propagation for the X-ray beam. However, as pointed out in the introduction, the passage of X-rays through a polycapillary affects the spectral distribution of the polychromatic beam. Indeed, the X-ray absorption by the polycapillary material cannot be neglected and it acts in a selective way as a function of the photon energy removing the softer energetic components more effectively. On the other hand, the harder components, which are characterized by smaller critical angles for total external reflection, have a lower probability to be in the reflection conditions when they impinge on the capillary walls and, therefore, are transmitted out of the lens side (leaving the main beam) more often. For this reason, the hard portion of radiation (escaping outside the capillary) produces the first contribution (the second is discussed later) to the so-called "halo" behind a polycapillary itself. As a consequence of these phenomena, the energy distribution of the photons results modulated upon propagation through the polycapillary. Therefore, the polycapillary acts as a bandpass filter, cutting the lateral sides of the spectral profile, as predicted theoretically in Section 1.

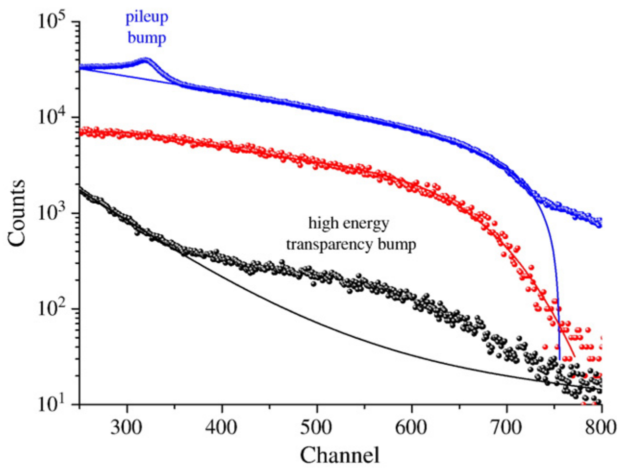

Fig. 3. Spectra corresponding to the primary beam as emitted by the X-ray tube (red circles); after the insertion of the cylindrical polycapillary between the tube and the detector (blue circles); after the insertion of the half-lens (black circles). The *x* axis in expressed in channels, the natural unit of a multichannel analyser. The amplification is set in such a way that each channel corresponds to 40 eV. The vertical scale is in arbitrary logarithmic units. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

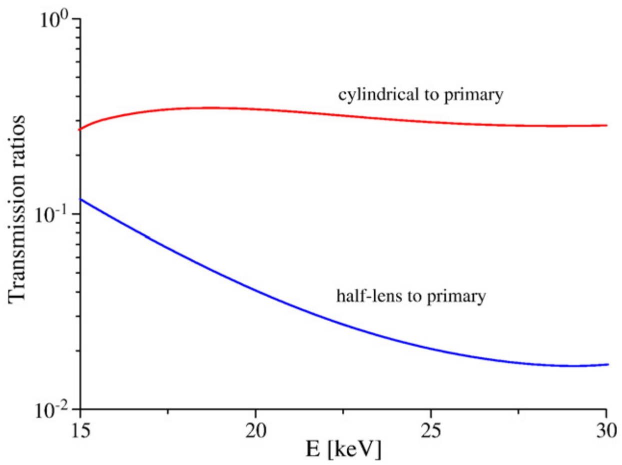

Fig. 4. Ratios between: (a) the spectrum taken after the insertion of the cylindrical capillary and the spectrum of the primary beam (red line); (b) the spectrum taken after the insertion of the half-lens and the spectrum of the primary beam (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In Fig. 3 the energy spectrum of the primary X-ray beam emitted by the tube anode measured by a solid state energy dispersive spectrometer, is shown (red circles).

The other two plots drawn on the same graph represent the spectra obtained by inserting, in turn, two different polycapillaries between the tube and the detector: a pillar formed by cylinder shaped channels (blue circles) and a half-lens (black circles).

Some spurious features can be noticed in the last two spectra. In particular, the pillar spectrum is affected by the presence of a hunch due to the pile up effect in the channel range from 250 to 350 (corresponding to 10–14 keV). Indeed, when the X-ray intensity is high in a certain spectral interval, the detector may not be able to analyse the photon separately. This happens in correspondence of the tube anode fluorescence lines (not visible because below the lowest channel reported in the graph), where the count rate is very high. In this case, the signals produced by two photons having energies E_1 and E_2, respectively, may appear as a single signal that the multichannel analyser associates to an unique photon of energy (E_1+E_2).

On the other hand, the half lens exhibits a broad bump at the end of the spectrum (see Fig. 3). It is produced by an imperfect alignment of the lens axis with respect to the propagation direction of the beam (second contribution to the aforementioned "halo"). The contribution of the misalignment is due to the photons that, instead of being guided by the capillary channels, reach the detector crossing the lens (see Fig 4). Since the penetration is bigger at the higher energies, both because the capillary material is more transparent in this range and because the critical angle is lower, the contribution of the transmitted photons is particularly evident in the high energy tail.

For these reasons, suitable fits are required to reconstruct the correct spectral profiles from the experimental data. Such fits (shown in Fig. 3) have to be used in the following calculations instead of the raw data.

After being normalized to the collection time and being fitted to remove spurious effects, the energy spectra collected by interposing the capillaries are compared with the spectrum of the primary beam in order to observe their effect on the transmitted radiation. In Fig. 4, the energy-dependent ratios are shown. These curves are obtained normalizing the X-ray beam intensity measured after the half-lens (blue curve) and the cylinder shaped pillar (red curve) to the primary beam. The red curve is characterized by a small reduction of the transmitted intensity at both the low and the high energies. Therefore, the cylinder shaped pillar acts as a band pass filter, as expected, but the effect is not dramatic. On the contrary, the high energy components of the blue curve are strongly reduced, showing how the half-lens focusing devices depress a fundamental part of the polychromatic radiation to use as primary beam in Energy-Dispersive X-rays Diffraction or Reflection experiments. Nevertheless, the reduction effect (although rather strong) is less serious than expected theoretically, since no sudden drop of the transmitted intensity is observed (compare Fig. 4 with Fig. 1).

An increase of the electronic density of the capillary walls material (for instance by doping the glass with heavy elements like lead), on one side, would reduce the penetration effect of the high energy photon; on the other side, would increase the refraction index and, as a consequence, the critical angle for total external reflection. Both these effects would concur to the reduction of the halo, that disturbs the Energy Dispersive measurements, while the latter would guarantee a higher transmission of the hard radiation inside the capillaries channels.

4. Conclusions

For what was discussed, polycapillary lenses are the ideal candidates to overcame some of the main problems of laboratory X-ray instruments, namely the low photon flux and collimation. Their application appears particularly promising in the case of the ED techniques that make use of polychromatic X-ray beams. Indeed, they are able to manipulate X-rays of different energies preventing chromatic aberration effects. Test measurements of their effect on a white beam, typically used as primary beam in ED experiments, showed a remodulation of the spectral less severe than that expected theoretically. The results indicated that polycapillaries actually remove the side bands of the spectral profile but with a smooth, rather than a sharp, cut. Furthermore, this effect will be further reduced in the future, optimizing the polycapillary optics for the energy range by means of glassy materials containing heavier elements.

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