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Synchrotron radiation-induced x-ray microanalysis

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Abstract

The qualities and limitations of synchrotron radiation-induced x-ray microfluorescence (SRXRF) spectrometry are discussed in comparison with those of more conventional microchemical techniques such as secondary ion microscopy and electron probe microanalysis. Examples of the analysis of particulates and the two-dimensional mapping of elemental species are given. Two new developments in connection with SRXRF are discussed: the use of microscopic x-ray absorption spectrometry and the predicted performance of SRXRF spectrometers installed with third-generation synchrotron sources.

Keywords: X-ray fluorescence spectrometry; Synchrotron radiation

Synchrotron radiation-induced x-ray microfluorescence (SRXRF) spectrometry is the microscopic analogue of the well established multi-elemental bulk analysis method of (energy-dispersive) x-ray fluorescence (EDXRF) spectrometry. In the latter method, radiation from bremsstrahlung tubes or radioactive sources is employed to induce emission of element-specific radiation by sample atoms; usually sample areas of 1–2 cm^2 are irradiated to yield (in the case of EDXRF) detectable count rates in the range 10^3–10^4 counts s^{-1}. To achieve the same count rate when an area of only, e.g., 100 μm^2 (10^{-6} cm^2) is employed, x-ray sources that are typically 10^6 times more intense are required. Such extremely intense x-ray fluxes are provided by electron storage rings where radiation is produced by forcing a beam of light elementary particles (electrons, positrons) in a quasi-circular orbit. At the location where the relativistic particle beam is forced to alter its direction by means of suitable magnetic fields, an intense beam of polarized, polychromatic radiation is produced in a cone oriented tangentially to the particle beam path. The vertical opening angle of the cone (typically a few mrad) is related to the energy of the circulating particles which is in the range 0.1–10 GeV. The maximum intensity is emitted in the plane of the storage ring itself. This radiation is linearly polarized in the plane; slightly above and below the storage ring plane, the radiation is elliptically polarised.

Typical energy distributions of the x-rays produced at bending magnets are shown in Fig. 1. In addition to bending magnets, other magnetic structures called wigglers and undulators are employed to produce even higher x-ray fluxes. These devices operate by forcing the particle beam into multiple oscillatory trajectories and are installed in the straight sections of the storage rings.

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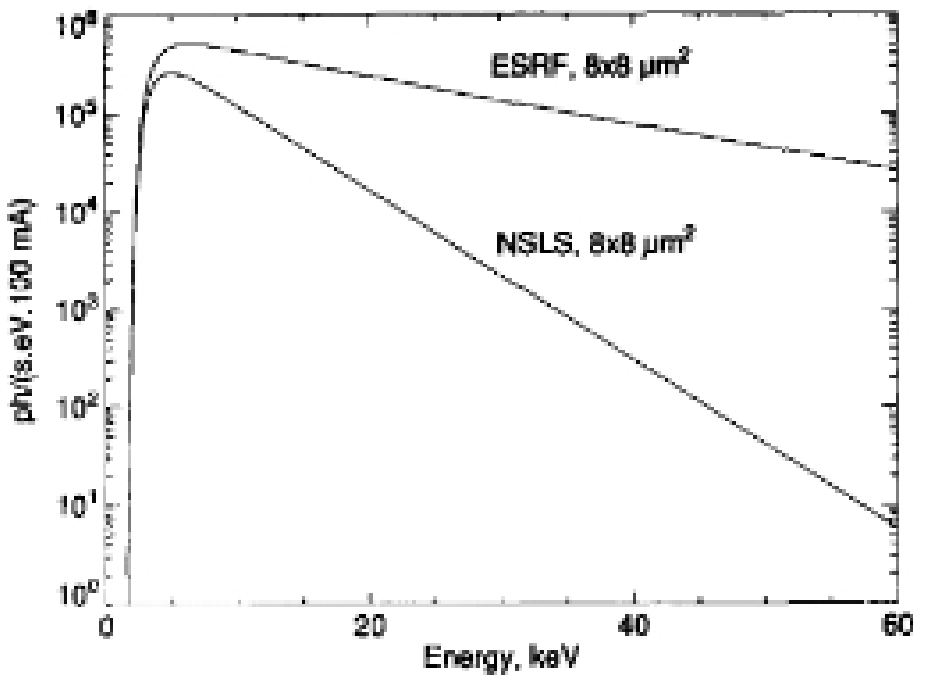

Fig. 1. Photon flux available at (0.8-T) ESRF and NSLS bending magnet beam lines using a 8×8 μm^2 pin hole collimator at 30 and 10 m, respectively, from the tangent point.

In the last 5 years, as a result of the increasing availability of electron storage rings as sources of highly intense, collimated and polarized x-rays in the energy range between 1 and 30–40 keV, a number of x-ray fluorescence microprobes have been constructed. An overview of some of the characteristics of these instruments is presented in Table 1.

The analytical properties of the various instruments are mainly determined by two factors: the characteristics of the storage ring/x-ray source at which they are installed and the way in which radiation originating from the ring is transformed into a microbeam. At Hasylab (Hamburg, Germany) [1] and the NSLS (Brookhaven National Laboratories, Upton, NY) [2], white light microprobes are in operation; at these stations, collimated pencil beams are used to perform sensitive trace element mapping with minimum detection limits (MDLs) in the 1–10 ppm range and with a lateral resolution of the order of 10 μm. At SRS (Daresbury, UK) [3], SSRL (Stanford, Ca) [4] and the Photon Factory (Tsukuba) [5], focused monochromatic microbeams are employed. Some of the optical configurations listed in Table 1 have only very recently been tested in practice and the analytical qualities of the corresponding SRXRF spectrometers still need to be evaluated [6,7].

In their most recent biannual review of x-ray spectrometry, Török and Van Grieken [8] considered the availability of intense small-sized beams for use in XRF experiments as one of the major developments in x-ray spectrometry, in addition to the use of laser-plasma sources, ultra-trace analysis by total reflection XRF (TXRF) and structural analysis by means of extended x-ray absorption fine structure (EXAFS) [9].

Most microanalytical methods such as secondary ion mass spectrometry (SIMS), proton-induced x-ray emission (μ-PIXE) and electron probe x-ray microanalysis (EPXMA) combine a number of useful qualities with one or more undesirable properties. This also applies to SRXRF. However, SRXRF also represents a unique combination of advantageous properties that are not found elsewhere. Similarly to SIMS, SRXRF is capable of trace level microanalysis but does not have any of the disadvantages asso-

TABLE 1

Characteristics of currently operating X-ray microprobes

Storage ring	E_c (keV) [a]	Optical system	Energy (keV)	Spot size (μm^2)
DCI	1.9	Curved graphite crystal	8–20	–
		Bragg–Fresnel lens	10	2 × 2
Hasylab	31.7	Pin hole	White	3 × 3
		Conical capillary	White	?
NSLS	5	Pin hole	White	5 × 5, or larger
Photon Factory	1.9	Wolter	10	3 × 10
SSRL	2.0	KirkPatrick–Baez	10–20	3 × 3
VEPP-3	5.4	Channel-cut monochromator	10–60	–

[a] E_c = critical energy of electron storage ring.

ciated with a destructive mass spectrometric technique. In addition to the damage that is inflicted by an ion beam on a sample surface, another significant disadvantage of SIMS is that the collected secondary ion intensities are very difficult to quantify; the use of elaborate empirical calibration procedures is required in order to do so. This calibration problem arises mainly as a result of the very complicated processes that give rise to the formation of the secondary ions. In contrast, the interaction of x-ray photons with matter is relatively simple, very well known and analytically describable. The combination of the capability to perform sensitive elemental mapping with the proven accuracy and reliability of quantitative XRF makes SRXRF a very interesting analytical technique.

Some of the weak and strong points of SRXRF can be understood when SRXRF is considered in comparison with its closest analogues, μ-PIXE and EPXMA. Essentially, these three methods differ only in the type of energy carriers that are being used in the micro beam. In all instances, the energetic particle is used to eject a core-level electron from a target atom, while the intensity and energy of the resulting characteristic radiation are measured with an Si(Li) detector. The overall efficiency of photon-induced x-ray emission (i.e., the number of characteristic photons produced per primary photon) is 10^2–10^3 times higher than in the case of electron- or proton-induced emission, and this quantity increases with increasing atomic number [10]. Accordingly, SRXRF is more suitable than EPXMA or μ-PIXE for trace determinations of the heavier elements (atomic number $Z > 20$–25). Also, per characteristic photon produced, the energy deposited in the sample using SRXRF is a factor of 10^2–10^3 lower than in EPXMA; the difference is even larger with μ-PIXE [11,12].

In addition to the production efficiency for characteristic radiation, the MDLs achievable with an x-ray-based technique are also determined by the importance of the continuous background in the collected EDXRF spectra. In this respect, another important difference between the interaction of photons and charged particles with matter is the probability of scattering interactions. As a result of many (in)elastic collisions, the retardation of energetic charged particles in solids gives rise to a bremsstrahlung continuum. In the case of x-ray fluorescence, each primary photon either does not undergo any scattering interaction at all or (in the worst case) encounters one or two (in)elastic collisions with sample atoms before it is either absorbed (photoionization) or escapes from the solid. Accordingly, nearly background-free XRF spectra can be obtained when monochromatic photon excitation is employed, yielding (sub-)ppm level detection limits for selected elements (see Fig. 4). Only in the region at or just below the primary energy do (in)coherent scatter peaks contribute significantly to the background.

Owing to the linear polarization of the synchrotron radiation in the storage ring plane, a further decrease in the scatter background level can be realised if the detector is also positioned in this plane and at 90° to the incident beam. As shown in Fig. 4, this effect makes it possible to achieve ppm MDL values with SRXRF employing polychromatic excitation [2].

An additional advantage of an x-ray microprobe (XRM) is that it can be operated in air or in an inert gas atmosphere such as helium; also, samples need not be conducting. A weak point of an XRM is its limited lateral resolution (see Table 1). This property is directly related to the currently attainable beam sizes but is also influenced by other factors (see next section).

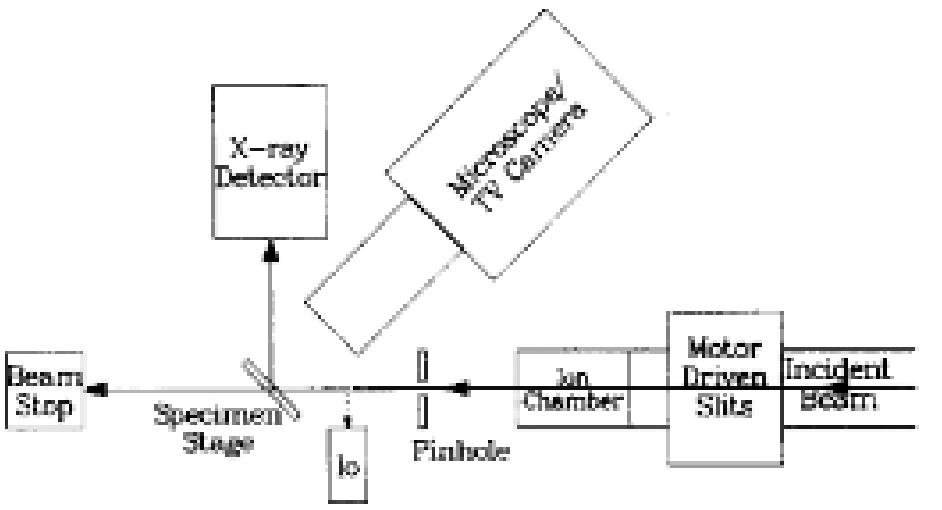

Fig. 2. Schematic diagram of the NSLS XRM. The pin hole–sample and sample–detector distances are of the order of a few cm.