

Lecture 2

Synchrotron Radiation and X-ray Fluorescence Spectroscopy

Synchrotron radiation (SR) was observed for the first time in April 1947 at General Electric in an advanced type of accelerator, an electron synchrotron [1]. While initially it was considered a nuisance, in the 1950s it became clear that the source of energy loss and annoyance for accelerator designers might become a very useful source of x-ray with potential applications in material science [2].

In the second lecture, several topics will be discussed in details such as; what is Synchrotron Radiation, advances in development of Synchrotron facilities including examples and basic components of a SR facility, but this chapter will mainly focus on one aspect of application of synchrotron radiation, namely X-Ray Fluorescence spectrometry, quantification and energy selective fluorescence spectrometry.

2.1. What is Synchrotron Radiation?

When electrons or positrons moving at relativistic speed (i.e. close the velocity of light) are subjected to a magnetic field, the trajectory follows a circular orbit and the SR is emitted in the tangential direction. The energy of the SR covers a broad spectrum with a peak at the so-called critical energy E_c , which is proportional to the electron energy E and inversely proportional to the radius of the trajectory ρ , according to:

$$E_c (keV) = 2.218E^3 (GeV)/\rho(m) \quad (2.1)$$

As an example, the brilliance of the SR generated in a bending magnet in SPring-8 is shown in Fig. 2.1.

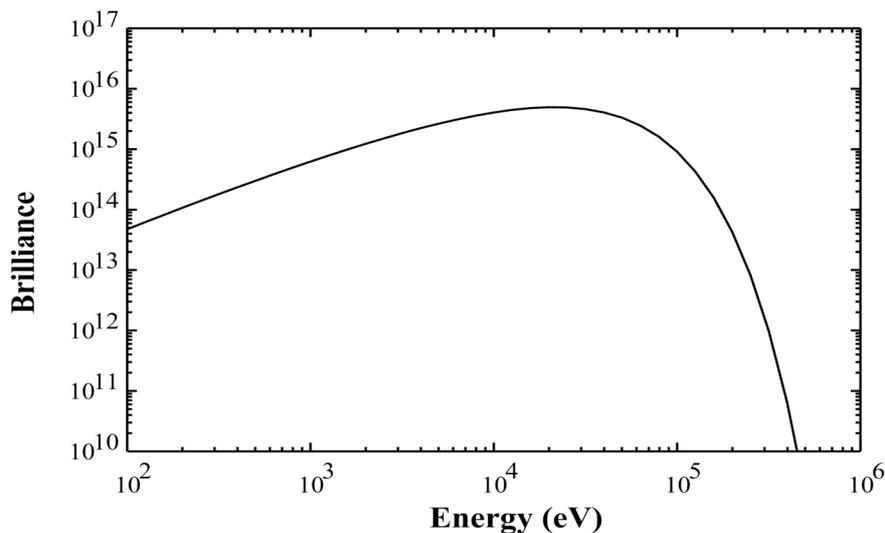


Fig 2.1. Calculated brilliance versus photon energy for the bending magnet in SPring-8. The unit of brilliance is photons/sec/mm²/μrad²/0.1% beam width.

What makes the x-ray from a Synchrotron Radiation source so useful leading to their wide use in physical, chemical and biological field are its unique properties of:

1. Tunability in incident x-ray energy

The absorption coefficient of an element is influenced by the chemical states of the substances, giving rise to the analytical method XAFS-x-ray absorption fine structure spectroscopy. Using this feature, the information of chemical state of elements can be obtained.

2. High photon flux

The emitted radiation has high intensity, 10000 times higher than conventional x-ray tubes. This feature results in high efficacy by reducing the measurement time.

3. High collimation

The highly collimated SR is suitable for micro analysis. This feature enables analysis of trace metallic elements contained in a biological specimen at a single cell level.

4. Pulsed time structure

Photons radiated from bunched electrons running periodically in the storage ring are pulsed at controlled intervals. This feature makes it possible to perform time-resolved measurements.

5. The radiation has a selective distinct linear or circular polarization

These features make the SR, in many cases, the only means of localized, non-destructive analyses of materials with extremely low concentration and thus most suitable for biological samples application.

2.2. Advances in the Development of Synchrotron Facilities

2.2.1. Examples of SR Facilities

Early in the SR history, SR researches were performed in a “parasitic” facility of a high current accelerator laboratory for high-energy or nuclear physics (the first generation). The 1980s saw the design and construction of dedicated, the second generation, SR facilities. In 1990s the third generation facilities were developed, using optimized magnet lattice and insertion devices in order to obtain more beam brilliance than bending magnets. The third generation SR facilities can generate $10^{11\sim 12}$ times higher brilliance than laboratory x-ray tubes.

(1) Photon Factory (PF)

Photon Factory (PF), High Energy Accelerator Research Organization (KEK), a second generation facility, started experiments in 1983. In PF, electron energy in the storage ring is 2.5 GeV and maximum current is 400 mA.

(2) SPring-8

SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), a third generation synchrotron radiation facility, opened for research in 1997. SR facilities consist of linear accelerator, storage ring, beam lines, etc. One of the most important part which determines the characteristics of SR is electron or positron storage ring. In SPring-8, the electron energy in the 1.5 km circumference storage ring is 8 GeV, and the maximum current is 100 mA. SPring-8 is equipped with advanced high performance insertion devices, resulting in high brilliance as high as 10^{20} photons/sec/mm²/mrad² in 0.1 % beam width. These high fluxes of photons make it possible to analyze ultra trace elements contained in a small area in biological tissues.

2.2.2. Basic Components of an SR Facility

SR facilities typically consist of an injection system, a storage ring and beam lines. In the injection system, electrons are generated, pre-accelerated, and sometimes a second accelerator further accelerates these electrons to more than 1 GeV before injection into the storage ring.

In the ring, bunches of electrons periodically circulate at relativistic speed for periods of up to many hours. The storage ring consists of radio-frequency (RF) cavities, bending magnets, other magnets, insertion devices and other control systems.

Most of the experimental results which will be presented in these lectures were obtained in two synchrotron radiation facilities in Japan: Photon Factory (2nd generation) and SPring-8 (3rd generation). The characteristics of the SR beam and beam lines of these facilities are representative of SR facilities worldwide. The basic components are briefly described below:

1. RF Cavities

The RF cavity system restores energy which the electrons lose because of the emission of SR, and stabilizes the bunch of electrons by phase-stability principle. The frequency of acceleration voltage is fixed to an integral multiple of the orbital frequency. The electrons exhibit longitudinal oscillations around the reference center of the bunch (called synchrotron radiation), and the bunch of electrons that are accelerated together is stabilized.

2. Bending Magnets

The bending magnets bend the trajectory of electrons and force them to circulate in orbit. Synchrotron radiation is emitted when an electron received centripetal force in the magnetic field of the bending magnet. Synchrotron radiation emitted from an electron traveling at almost the speed of light is highly collimated by relativity effect. The magnitude of the relativistic angular width of the bending magnet radiation ($\Delta\psi$) is given by:

$$\Delta\psi = 1/\gamma \quad (2.5)$$

The critical wavelength is given by:

$$\lambda (c) = 18.64 / (B * E^2), \quad (2.6)$$

where B (the magnetic field) in Tesla and E (the beam energy) in GeV. One-half of the power is radiated above and one-half below the critical wavelength.

3. Insertion Devices

Higher intensity synchrotron radiation is produced by an insertion device. The insertion device is comprised of a periodic array of dipole magnets with alternating polarity. According to the magnitude of the oscillation of the electron trajectory, there are two types of insertion devices, a **Wiggler** and an **Undulator**.

a. Wiggler

In a **wiggler**, a sequence of bending magnets with relatively weak magnetic field result in small deflection angle ($< \gamma^{-1}$), and the interference effects produce a radiation which has a continuous spectrum with higher fluxes and with short wavelengths. The wiggler is often used as sources in order to increase the flux at shorter wavelengths. A sequence of bending magnets with n poles of alternating polarities can enhance the flux by $2n$ times (the upper smooth curve of Fig. 2.2.). The critical wavelength for a wiggler is lower than that of a bending magnet.

b. Undulator

In an **undulator**, a periodic array of strong magnets resulting in a large deflection angle ($>> \gamma^{-1}$), and the coherent interference effects produce highly collimated radiation, which has one or a few spectrally narrow peaks (a fundamental and harmonics). For n poles, the beam's opening angle is decreased by $n^{1/2}$ and thus the intensity per solid angle increases as n^2 (the upper curves of Fig.2.2).

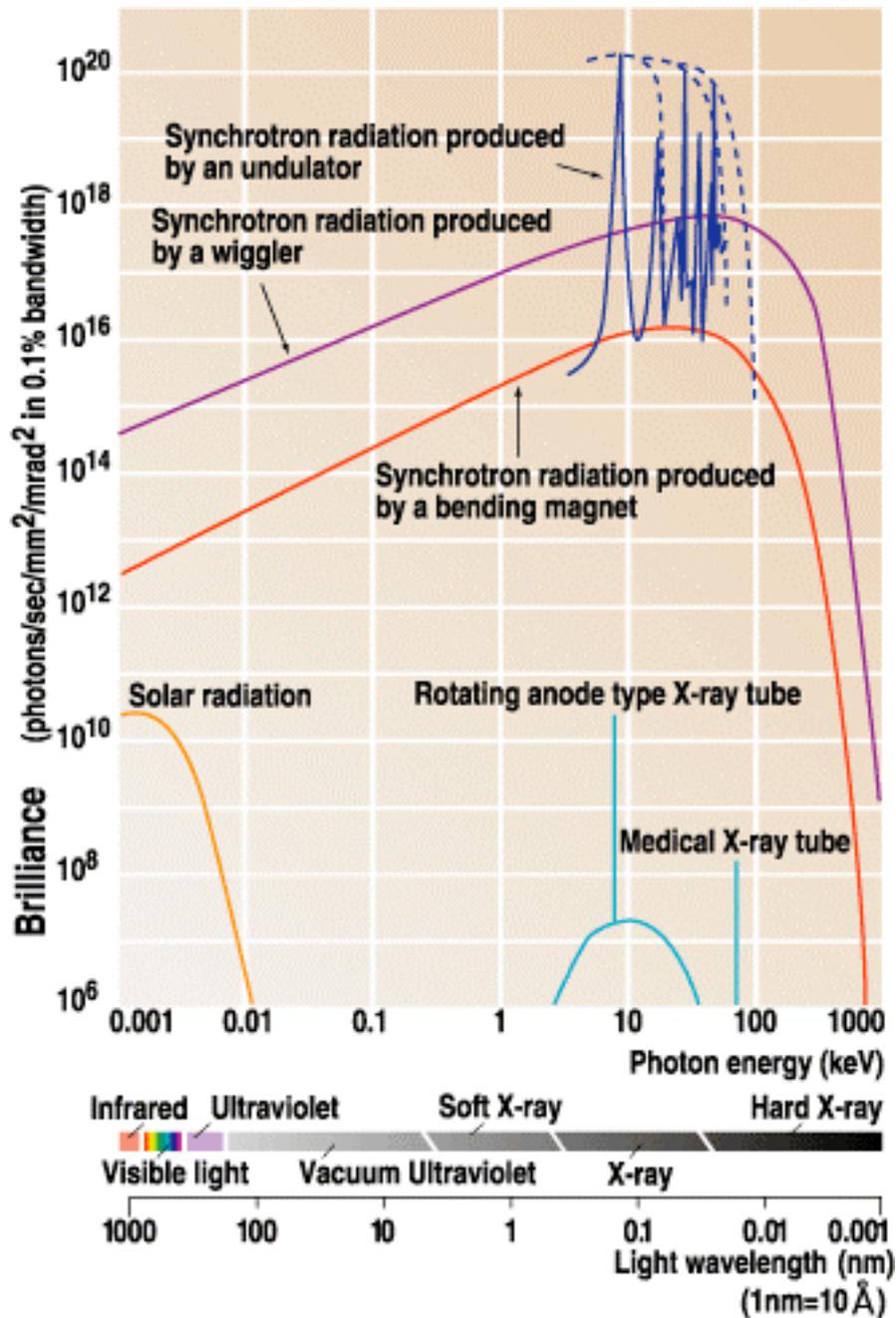


Fig. 2.2. Comparison between the light from synchrotron radiation and that from the conventional X-ray source.

4. Monochromator

A **monochromator** is used to select a very narrow energy band of the spectrum and a focusing system (e.g. Kirkpatrick-Baez mirror system) can be used to obtain sub micron beam diameter. A synchrotron radiation beam can thus be within a few microns in size and can have a variable (tunable) energy.

5. End Station

The **end station** consists of instruments for introducing samples to the beam and associated detectors for measuring the original and fluorescent radiations, including instrumentation to control the end station and measuring the response of the detectors.

With the availability of hard x-ray radiation even large pieces (several cm³) can be investigated. By tuning the energy of the x-rays one can further adjust the penetration depth and thus achieving surface or bulk sensitivity. Varying the incidence to grazing angles, the x-ray beam can be used as a surface probe. Because of the very small divergence, it enables investigation of thin layers or coatings. The high intensity allows very fast data acquisition, which in turn enables measurements to be carried out during processing of the material under investigation. These in-situ experiments provide information about the dynamics of processes, which take place during the transformation of the sample. The large penetration depth of x-rays facilitates the study of samples in different sample environments such as furnaces, cryostats, pressure or chemical cells.

2.3. Synchrotron Radiation X-Ray Analysis (SR-XRF)

The Synchrotron Radiation X-Ray source represents a great improvement in x-ray production technology [5]. By using Synchrotron Radiation for XRF analysis, many researchers can make measurements with improved sensitivity and spatial resolution. The major features of SR-XRF analysis are as follows:

- (1) local area analysis by using micro beam
- (2) possible to measure in the air or water
- (3) non-contact and non-destructive assay
- (4) rapid measurement
- (5) precise assay for the trace elements.

especially, the features of (2), (3) and (5) are superior to the other elemental analysis techniques.

2.3.1. Fluorescence X-Ray

By means of μ -XRF analysis using synchrotron sources, it is possible to collect information on the distribution of trace constituents of a material with high lateral resolution. In view of the high sensitivity for heavy elements, synchrotron radiation induced μ -XRF is particularly valuable for the trace-level microanalysis of the heterogeneous geological materials and the biomedical samples [6].

The generation of the fluorescence x-ray is caused by the excitation of an inner shell electron and the transition of another electron from an outer shell to this vacancy. Energy release takes place either by emission of an Auger electron, or by a quantum of the so-called characteristic x-ray. The de-excitation of an atomic shell is characterized by the **fluorescence yield**, which is defined as the number of characteristic x-rays per primary vacancy emitted from this shell. The corresponding **Auger yield** is defined as the number of Auger electrons emitted per primary vacancy from the shell.

2.3.2. Detectors

The fluorescence x-rays emitted by an atom after absorbing the synchrotron radiation are measured in detectors for quantitative analysis. The most commonly used x-ray detectors are, the proportional counters and solid-state ionization detectors namely scintillation detectors, Si(Li) detectors and charge coupled devices. The detectors measure the x-rays energy spectrum, specifically the characteristic x-rays, whose intensities are proportional to the concentration of the elements in the sample. Solid state detectors are energy dispersive detectors, where the x-rays are absorbed and converted to electrical signals proportional to their energy. These detectors usually have good energy resolution, defined as that required to resolving the different characteristic x-rays. The proportional counters can be operated in an energy dispersive mode but the energy resolution is usually not adequate. In order to improve the resolution, the proportional counter is used as a detector only in a Bragg crystal spectrometer, where the energy dispersion is carried out by Bragg filters. This detector system is called the wavelength dispersive spectrometer, and is particularly suitable for lower energy x-rays (< 20 keV).

Solid-state detectors cover a wide energy range (1-100 keV and higher) and provide a large solid angle of detection. The latter is very important in analysis of extremely small amounts of materials. For energies higher than 20 keV, wavelength-dispersive systems are not very effective and the SSD is the most convenient device to detect the K lines of heavy elements [8].

A solid state detector is essentially a reverse biased diode with a wide junction (to a few mm) of carrier free, depleted layer created by compensating p-type material with n-type donors such as Li. Li drifted Si detector, Si(Li) for short, is the most commonly used type, and lately inherently intrinsic Ge detector is also used for x-ray spectrometers. In these detectors, ionization by the x-rays in the intrinsic region produces electron-hole pairs which are swept by the reverse bias electric field to produce a current pulse. The number of pairs created is proportional to the incident x-ray energy. The charge collected at the anode is converted to a voltage by an amplifier. These are subsequently converted into voltage pulses by a preamplifier, and further amplified and shaped by a linear amplifier to optimize the signal-to-noise ratio. The signals are then fed into a multi-channel pulse height analyzer to be sorted into an energy spectrum. Solid state detectors are stored in liquid nitrogen to prevent the diffusion of lithium of the depletion layer in the Si(Li) case, and to reduce the noise in general.

In the simplest form of data acquisition, a certain range of energy corresponding to the characteristic x-ray for an element can be selected using a single channel pulse height analyzer (SCA). X-ray line scans and x-ray maps for the element can be obtained by recording the intensity of this energy window as a function of the sample coordinates

2.3.3. X-Ray Fluorescence Spectroscopy: A typical spectrum

A typical X-Ray Fluorescence spectrum is shown in Fig. 2.3. The y axis (ordinate) shows the intensity (total counts per channel in the multi-channel analyzer, MCA) as a function of the energy (x axis, abscissa) of the detected x-ray. The sample measured here is a very thin specimen (about $6\ \mu\text{m}$) of a brain tissue. The x-ray beam is $10\ \mu\text{m}$ in diameter. The relevant elements are marked on each peak corresponding to the characteristic x-ray peaks of that element. A table of the characteristic x-ray energy of the elements (K_{α}) is cited by J.W. Mayer and E. Rimini [9]. The height of the peaks, more precisely the area under a peak, is proportional to the concentration of the element in the specimen. A careful examination of the spectrum shows that the peaks representing each element are superimposed on a “back ground” signal.

The spectrum usually contains a number of spurious discrete components, appearing as peaks, namely the sum peaks (also known as pile-up peaks) and the escape peaks.

1. **Sum peak:** A peak that appears at an energy that corresponds to the sum of two or more other peaks' energies. A sum peak occurs from summing of the electrical pulses at high-count rates because the individual nuclear or electronics events occur within a time period that is less than the resolving time of the amplifier. Therefore one count is lost from each peak and is added to the sum peak.
2. **Escape peak:** A peak displaced at the lower energy side by a well-defined amount. The escape peak arises from the escape of the K x-ray of detector material. For Si detectors is expected to appear at the channel corresponding to energy $(E - 1.74)$ keV. The escape peak is typically less than 1 % of the peak of the element of interest.

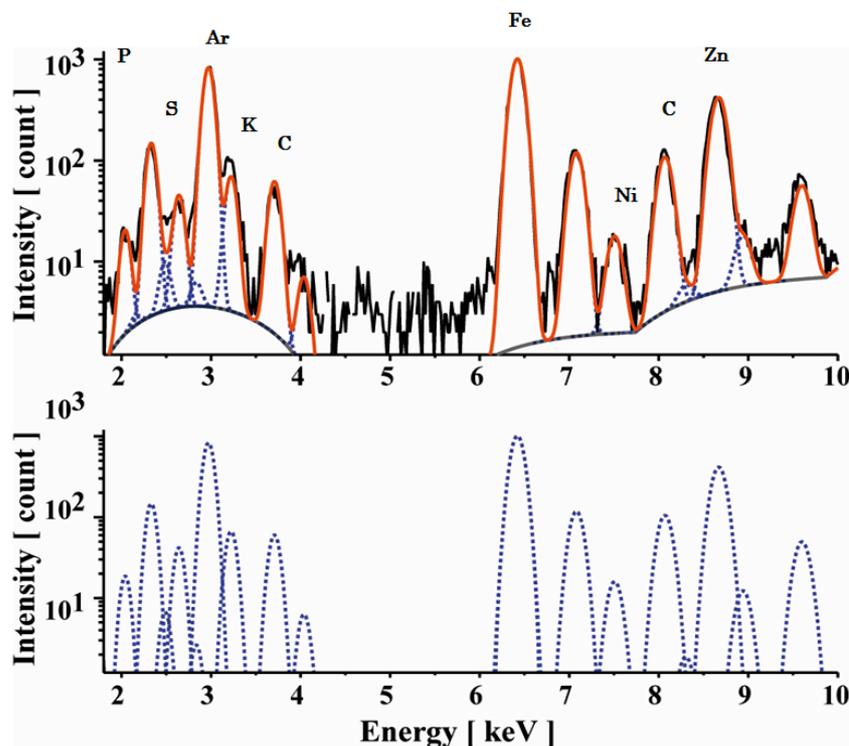


Fig. 2.3. Typical XRF spectra.

2.3.4. Background Level in Detected Spectrum

2.3.4.1. Basic components of the background in SR-XRF

The interaction between the exciting radiation source and a substance has complicated properties because of a variety of components added to the sample emission spectrum. When the incident x-ray beam has a large flux of quanta, the complicated factors are the spectral density of the background in the region of the lines being analyzed and the counting rate of the detector that mainly determine the analytical sensitivity. In the most common case of excitation by monochromatic radiation of samples with a light-element matrix, the background has the following forms:

- (1) a peak from the elastic scattering of the exciting radiation;
- (2) a peak from the Compton scattering of the same radiation (single for thin samples and multiple for thick ones);
- (3) escape peaks of detector fluorescence emission, spaced from the elastic and Compton peaks as well as from the rather intense spectral lines of the sample at the energy of the fluorescence quantum emission of the detector material (9.9 keV for Ge K_{α});
- (4) escape peaks of detected quanta, Compton-scattered in the detector at an angle of about 180° and leaving it along the shortest path. In this case, the detector registers the recoil electron alone. When there are many intense lines in the spectrum of a sample or when the detector is of insufficient thickness, the indicated peaks form a continuous background in the low-energy region [8].

2.3.4.2. Compton scattering

An electromagnetic wave has properties as both the wave and particle. In the energy region of x-ray, it tends to display the property as a particle. In the process of inelastic scattering by free or comparatively weakly coupled electrons in a substance, x-ray quanta lose some fraction of their energies. The incident x-ray is scattered as one with a little longer wavelength. This phenomenon is called Compton scattering. If the direction and detection solid angle are optically chosen, the application of the polarized synchrotron radiation enables the intensity of this process to be considerably reduced (by a factor of 10-100) and, thus, the sensitivity to be improved, or the measurement time to be shortened using XRF technique.

2.3.4.3. Elastic scattering

The electrons of a substance are forced to oscillate by incident x-ray. The subsequent emission of x-ray with the same frequency is caused by their oscillations. This phenomenon is called elastic scattering. The atomic nucleus of a substance is forced to oscillate by incident x-ray, too. However, it is generally neglected because of its weak amplitude. With excitation by the white or wide-band SR beam, the elastic scattering can become the basic background below the analytical peak of a spectrum if the cross section of the elastic scattering towards a SSD starts to exceed the Compton scattering. With monochromatic excitation the peak from

the elastic scattering lies outside the detected emission lines of elements and can influence the analytical sensitivity, creating an additional load for a SSD and a spectrometric amplifier. In this case, the effect will be significant if the elastic-scattering cross section becomes larger than or comparable to the Compton-scattering cross section [8].

2.3.4.4. Bremsstrahlung radiation of photoelectrons in the sample

Under the interaction of the exciting radiation and a sample, a certain number of photoelectrons appear and are decelerated in the sample volume, as a result of the photo effect. During their decelerations, there appears radiation with a continuous spectrum lying within the $E_\gamma \leq E_e$ range of energies where E_e is the energy of the photoelectrons. Among the major factors, it is suggested that limiting the ultimate sensitivity of the SR-XRF technique is the bremsstrahlung radiation background under the analytical peaks [8].

2.3.4.5. Improvement to reduce the background

It is suggested that the presence of the natural SR polarization is the most important qualitative advantage of SR for the x-ray fluorescence analysis process over the other types of x-ray radiation. The plots of the elastic and inelastic scattering of the exciting radiation have a minimum that is depended on the mean polarization coefficient, the selected value of energy and the angular opening of collimators in the detection system. The decrease of the intensity of the elastically scattered and the Compton peaks can be realized by placing the detector in the plane of the E-vector of the monochromatic SR beam at an angle $\theta = 90^\circ$ to the beam and consequently improve the background plateau height of an incomplete charge collection in the SSD. In addition, the acceptable rate of counting the fluorescent lines grows because of the limited counting rate of a SSD.

If the emission spectrum has peaks in many orders of magnitude different in intensity, the excitation of some parts of a spectrum would better be done separately by varying the excitation conditions (monochromatic energy is set higher and lower than the K absorption edge of an element of high concentration). The selective excitation makes possible to suppress the heavy-element lines during detection of fluorescent quanta of lighter elements.

The use of the specific features of SR makes possible to reduce substantially the background below the analytical peaks and, hence, to improve the sensitivity and to shorten the time of analysis [8].

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