BNL--44768

DE90 013743

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**BASIC PRINCIPLES OF SYNCHROTRON RADIATION-INDUCED
X-RAY FLUORESCENCE (SRXRF)**

Received by OSTI

JUL 10 1990

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May 1990

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Prepared for Sincrotrone Trieste, Italy
Sincrotrone Trieste Internal Report

DEPARTMENT OF APPLIED SCIENCE

BROOKHAVEN NATIONAL LABORATORY

UPTON, LONG ISLAND, NEW YORK 11973

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BASIC PRINCIPLES OF SYNCHROTRON RADIATION-INDUCED X-RAY FLUORESCENCE (SRXRF).*

BNL-44768

Informal Report

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Abstract:

The characteristic x rays can be used as powerful analytical tools for qualitative and quantitative determination of the major, minor and trace composition of materials. X Ray Fluorescence (XRF) techniques used for almost four decade to solve many problems in basic, applied science, and in industry. The XRF techniques that were developed initially used crystal spectrometers, and are referred to in literature as Wavelength Dispersive (WD) techniques. These WD techniques are still used in many fields and have the merit of a excellent energy resolution that allows for the analysis of many elements while avoiding the overlapping of some fluorescence peaks. They are also particularly useful in a matrix that produces copious quantities of a particular radiation. The principal disadvantages of a WD system are the low efficiency of crystal and the reduced energy region in which crystal spectrometer can be used. In the 1960's, Solid State Detectors (SSD) were developed with energy resolution such that the Energy Dispersive XRF techniques could be developed. These SSD's overcame some of the limitations of the WD techniques. The most attractive characteristics of the EDXRF techniques are in their intrinsic multielemental and non destructive capabilities. The major limitation of the SSD's is that the poorer resolution means cannot discriminate all of the characteristic x ray peaks, especially that of the low Z elements. The development of the high intensity, high brilliance Synchrotron Radiation (SR) sources have open the possibility to make microanalyses using the XRF techniques, increasing the interest of the scientific community for these techniques. In this paper the basic concepts of the XRF technique are reviewed taking in account the availability of the new sources of x rays.

*Research supported in part by the US Department of Energy, Chemical Sciences Division, Office of Basic Energy Sciences, under Contract No. DE-AC02-76CH00016.

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I. FOREWORD

Soon after the discover of x rays attempts were made to investigate the characteristic x rays from the different elements. It worth remembering, that the theory of the atom as elaborated by Bohr and Sommerfeld at the start of this century, found an experimental ground for the explication of the x ray spectra [1]. In the last 50 years the characteristic x rays have been constantly used in all areas of science and engineering [2,3,4]. In the last three decades techniques have been developed using the Fluorescence of the characteristics x rays (XRF). These technique utilize the emission of the characteristic x rays from a target when irradiated with primary x rays. More recently, with the availability of radioisotopic sources, electron microscope and accelerators, techniques have been developed that use charged particle beams to produce the characteristic x rays, referred to as the x ray Emission (XE) techniques [5,6]. It is evident that the difference between XRF and XE is in the excitation process; a photoelectric interaction as opposed to an ionization process by electrons, protons, ion beams. In both cases the emitted characteristic spectra are the same. It worth pointing out that photonic excitation provides a chance to selectively excite and analyze a specific element (selectivity). This is not completely possible for excitation with charged particles.

XRF has been continuously used in physics research. As the technique has developed past the point of a physics novelty, the interest of pure physicists to improve the technique has progressively declined. In the meantime uses of XRF techniques have grown in chemistry, geochemistry, metallurgy, industry and, more recently, in biology and environmental sciences. Presently XRF is considered more important in other fields of the science and engineering than in physics.

The attraction of XRF is basicly due to the simplicity and the accuracy of the technique for analysis of elements in a sample. Because Photo-Electric (PE) cross sections that lead to the production of the characteristic x rays are large, XRF has sensitivity for the analysis of many elements down to trace levels. It is sometime useful to make a distinction between techniques that use a crystal spectrometer, which are referred to wavelength dispersive [2], and the others which use Solid State (energy dispersive) Detectors (SSD) [7]. The Energy Dispersive (ED) techniques are of great interest since the allow for the simultaneous detection of more than one fluorescent line while providing an efficiency that is at least one order of magnitude better than is available with a crystal spectrometer.

If medium and high Z elements are probed, there can be a "high" penetration of the characteristic x rays of through the sample. This allows for the use of these techniques in non-destructive analysis and in dynamic studies with stable tracers [8,9]. Another interesting prospect is to use characteristic x rays for tomographic studies [10].

In the case of charge particles (i.e., electrons and protons) the possibility to obtain a very thin pencil of particles has opened the door to microanalyses, which is very important for many applications. In principle microanalysis with photons is physically possible, but the strength of traditional sources have always limited the technique. Using electron synchrotron storage rings as the sources of radiation, referred to as SR, have improved the prospects of developing micro-XRF techniques since they not only have high intensities, but the synchrotron radiation is naturally collimated and has low divergence [11,12]. This is important since there is a substantial reduction of radiation damage [13] when compared to beams of charge particles. For other intrinsic merits of photonic excitation as opposed to charged particle excitation see [11]. Using SR as a source has other advantages such as its intensity and broad spectral interval and high degree of polarization of the beam. The high intensity opens the prospects for excitation with monochromatic radiation and the polarization can be utilized to reduce the spectral background from scattered radiation.

With high intensity monochromated photon beams, in conjunction with tunability, we can study the chemical states of elements by scanning the incident energy about the absorption edge and hence measuring energy shifts of the absorption edges. This is known as near edge XRF spectroscopy [14] or as chemical speciation. With little modification of a high resolution XRF system effects such as x ray resonant Raman scattering [15] can be investigated.

The aims of this note are (i) to provide the basic language of XRF, (ii) to show the possible advantages that one can attain using the different measuring strategies and (iii) review the equations on which the XRF techniques are founded. For simplicity we will consider monochromatic excitation, followed by a discussion of excitation with the continuous radiation. XRF with SR is presently being developed at several facilities throughout the world. Active groups exist at the NSLS, Photon Factory, Daresbury, DESY, Novosibirsk and Frascati [16,17,18,19,11,20]. Unlike tube generated x rays SR provides many opportunities for different approaches to XRF. While the existing programs have well established its capabilities and usefulness to the outside community, there are still many aspects left to investigate and develop.

II PRINCIPLES OF THE SRXRF.

The Synchrotron Radiation Induced X Ray Fluorescence (SRXRF) is based on fluorescing characteristic x rays with SR. There are two possible modes of excitation: a) using the "white" spectrum emitted by the electrons accelerated in the storage ring; b) monochromating the beam selects only a very small portion of the white spectrum is selected, while gaining tunability.

The photoelectric effect is the basic interaction whose consequence is in part the emission of characteristic x rays after excitation with an beam. The photoelectric effect is a two steps process in which (i) an electron from a inner shell (K,L,M,...) is removed and subsequently (ii) an or an Auger electron (depending on the fluorescence yield) are emitted. If the energy of the x rays is lower than the binding energy of the electron in one atomic orbit the photoelectric effect doesn't take place for that electron. As the energy of exciting radiation is increased, we pass through jumps in the photoelectric cross section.

FIGURE 1 Scheme of the most important transitions.

The probability for electron vacancy production is greatest for photon energies immediately above the threshold for the ejection of the bound electron. It then decreases approximately as $E^{-3.5}$. This energy dependence has important consequences when one wishes to analyze a wide range of elements using a single energy photon source. After a photoelectric interaction, the irradiated atom can emit x rays from the de-excitation. Of the excited states, the energies of the photons correspond to internal allowed transitions. In particular, the K-series corresponds to the transitions from the outer shells to the K-shell, whereas the L-series correspond to transitions to the L-shells and so on (see fig.1).

FIGURE 2 Schetch of a XRF measuring system.

Each atom has a characteristic set of x rays, the energy of which can be used for the identification of the element. A sample containing several elements will emit as many x rays of different energies as there are elements.

The intensity of a fluorescent lines depends on several fundamental physical parameters, such as the photoelectric cross sections (σ_{PE}) and the probabilities of the different internal transitions. If we consider, for simplicity, the case of a K line of a particular element, i , excited by a monochromatic beam of intensity I_0 to the intensity of this line (dI_i) coming from the layer dm (fig.2) can be written as:

$$dI_i = I_0 \left[\frac{N}{W_i} \omega_i \sigma_{PEi} \frac{S_k - 1}{S_k} \right] w_i dm \quad (1)$$

where (N/W_i) is the ratio of Avogadro number over the atomic weight of the element, S_k is the absorption jump edge of the k absorption edge w_i is the weight fraction of the element, ω_i is the fluorescence yield of the element and dm (ρdx) is the mass for unit surface of the target.

We will also introduce also the equations for the intensity of the scattered radiation that are the remaining part of the spectrum emitted by a target irradiated with x rays. For the coherent scattering the intensity is given by

$$dl_c = I_0 \left[\sum_i \frac{N}{W_i} \sigma_{c,i} \right] w_i dm \quad (2)$$

where $\sigma_{c,i}$ is the coherent scattering cross section for the element i in the target and w_i is its weight fraction. The coherent scattering is strongly forward peaked for light matrices it is a significant part of the total scattered radiation only for scattering angles lower than 30° .

For the incoherent scattering the total intensity of the band is given by

$$dl_i = I_0 \left[\sum_i \frac{N}{W_i} \sigma_{i,i} \right] w_i dm \quad (3)$$

where $\sigma_{i,i}$ is the incoherent scattering cross section for the element i in the target. It worth remembering that the incoherent (Compton) scattering have a distribution of energy whose maximum is at the energy:

$$E_c = \frac{E_0}{1 + \left(\frac{E_0}{mc^2} \cos(\theta) \right)} \quad (4)$$

the width and the actual shape of this band depends from a) the energy of the primary beam, b) the scattering angle (θ), c) the geometrical parameters of the measuring system and d) the composition of the sample. This scattered radiation limits the performance attainable with a XRF system either directly, through the increment of the spectral background, either indirectly through saturation of the electronics. Both these effects are more problematic in ED-XRF systems than in WD-XRF systems.

The basic principles of the XRF techniques can be treated starting from the fundamental equations that provide the intensities of fluorescent and scattered peaks. Tabulation of the fundamental parameters that appear in the equations 1-3 can be found in literature, in particular a) the mass absorption coefficients, the photoelectric cross sections and the absorption jump edge of absorption edges the can be found in [21], b) fluorescent yield in [22], the incoherent scattering functions and the atomic form factors in [23]. The study of these equations provide a thorough knowledge of the potentialities and of the limitations of

FIGURE 3 XRF spectra excited with: A) a monochromatized (16 keV) photon beam (0.01% bandwidth) at ADONE (Frascati) and B) with the continuous spectrum of the NSLS 2.5 GeV storage ring at Brookhaven partially filtered with 200 μm of Al.

the XRF techniques, using the different modalities of excitation and detection.

An XRF spectra resulting from excitation with monochromatic radiation, is constituted by discrete structures, the characteristic peaks, the coherent scattering peak and the incoherent scattering distribution, along with a continuous underlying component, namely the background (fig.3). This background is produced in part by process in the detector and in part by scattering events (radiative background) [24]. This is true with different mechanisms either for wavelength [25] as for energy dispersive techniques [24]. For the case of an excitation with a continuous (white) spectrum the background is preeminently radiative since there are no distinguishable coherent scatter peaks and incoherent scatter distributions (fig.3 B). One method to reduce the background around a photo-peak is to use in monochromatic radiation near the energy of the absorption edge of the element being probed. In doing this one should consider that the monochromatization reduces the intensity of the exciting radiation beam, and the spectral background is preeminently electronic (fig.3 A). Of course, this has the consequence of reducing the

intensity of the probing radiation. We must bear in mind that the final goal in the optimization of a XRF system is to maximize the signal of interest while minimizing the other signals. For state of the art SSD's the amount of information that can be processed without significant loss of energy resolution or/and an increase in electronic background is in order of 10^4 cts/s. That level of counting rate can be easily reached using x ray tube either with and without secondary target. Synchrotron radiation, with its orders of magnitude increase in intensity and its high degree of polarization can then be utilized to improve on the fluorescence information.

One advantage of using white radiation for excitation is the inherent multi-elemental analytical capabilities. In this case the background is due to the scattering in the sample that produces white secondary radiation. With monochromatic excitation in a light matrix, the predominant parts of the spectra are that incoherently and coherently scattered. In this case we can consider the spectral background as proportional to scattered peak intensity. In either cases, there is a straightforward dependence of the background on the total number of the photons detected allows us to make realistic models of the spectral background and an evaluation of the signal to noise (S/N) ratio [25].

In order to perform quantitative determinations of the elements in a sample of unknown composition it is necessary to accurately calibrate the system. In XRF techniques it is not necessary to calibrate with a standards of each element since the response is in general a smooth function. We then perform corrections that take in account several effects that change the intensity of characteristic peaks (1). When we attempt to relate the theoretical intensity to the total number of photons detected in a given interval of time, there are several factors that must be taken into account. First of all there are the physical (ϵ_p) and geometrical efficiency ($\epsilon_g = d\Omega/4\pi$) of the detection system. These efficiencies depend on the nature of the detector and on the solid angle subtended by the detector entrance window. There are the absorption effects that limit the throughput of the fluorescent photons from the target. The absorption effects can be subdivided in two part (i) the absorption of the primary beam in the target and in the material surrounding the sample being studied; (ii) the self absorption of the characteristic x rays in the sample. In order to estimate the absorption effects, the sample can be modeled as a very thin layer sheet with the primary beam impinging on one side (see fig.2). It is possible to see that the total number of counts detected (I_D) can be written as:

$$I_i = \epsilon_p \epsilon_g \int_0^T dt \exp(-K m) = I_f \frac{1 - \exp(-KT)}{K} \quad (5)$$

$$I_f = I_o \left[\frac{N}{W_i} \omega_i \sigma_{PE_i} \frac{S_k - 1}{S_k} \right] w_i$$

where $K = \left[\frac{\mu(E_o)}{\cos(\phi)} + \frac{\mu(E_f)}{\cos(\psi)} \right]$ and T (gm/cm²) is thickness of the layer and E_o, E_f are the energies of primary and fluorescent x rays.

The term in the square brackets of equation 5 is call the self-absorption factor. Its meaning can be easily clarify if we consider, as is true, that $1/K$ is proportional to the mean free paths of the primary and secondary radiation in the sample. When $1/K > T$ the absorption effects can be neglected because paths of the x rays in the sample are larger than the sample thickness. In this case the self-absorption factor can be considered as equal to T . If $1/K < T$ the self-absorption factor is equal to $1/K$. In this case the intensity is independent on sample thickness, i.e. the characteristic x rays coming from the inner layers are completely absorbed by the sample. Common jargon says that in the first case the conditions are that of a "thin sample", whereas in the latter are that of a "thick sample". We will refer to these two conditions in order to discuss the possibilities to use different targets, and the related limitations. Fig. 4 shows I_f/I_o as a function of T/K .

In writing the equations 1-5 we have implicitly assumed the

FIGURE 4 I_f/I_o vs T/K showing the self-absorption effect.

sample as homogenous. Looking now to the meaning of the self-absorption factor we see that the absorption effects depend from the size of the particles compounding the sample. It is evident that in the case of a particulate the absorption of the x rays depend not only from the total thickness of

the sample but also on the size of the particles, in particular a non uniform distribution of the element being analyzed can influence the intensity of corresponding characteristic peak. There are simple model to correct for non-uniformity of the sample

FIGURE 5 Spectrum of the SR filtered with 100 and 400 μm of Al.

tons generated in primary interaction. It is useful to make a distinction between enhancement effects that are consequent to the presence of a particular element in the sample, and effects which are a consequence of primary scattering (coherent or incoherent) events. In the first case there are two or three subsequent photoelectric interactions, of which the first pertain to an element with a characteristic x ray of energy greater than the absorption edge of the second one. In this case the effect can be regarded as a *inter-element effect*. Whereas in the case of a primary scattering event, the interaction is between the whole sample and the element. It is not easy to evaluate these enhancement effects. In particular for two or more photoelectric interaction there are quantitative estimations [26,27], but for multiple scattering events and for a scattering event followed by a photoelectric event, quantitative estimations needs to be based on Monte Carlo methods. It is easy to affirm that in a thin sample approximation these effects are always negligible. It is easy to see that the multiple photoelectric interaction constitute a problem only in particular situations such as the analyses of metal alloys and of some geological samples.

Two useful definitions are that of sensitivity and minimum detectable limit. The sensitivity is minimum change of weight fraction or mass for square centimeter of one element that can be measured. The sensitivity can be written as:

$$\Delta w_i = \frac{\sqrt{2} I_i}{dI/dw_i} \quad (6)$$

assuming a uniform distribution of particles of the some size [2].

A second class of problems concerns the *multiple interactions*, for example a Compton event followed by a photoelectric interaction. In this case it is possible to observe a reinforcement of the intensity of the characteristic lines, due to the excitation of the fluorescence by photons

Fig. 4 shows as the sensitivity progressively decrease passing from a "thin" sample to a "thick" sample.

The Minimum Detectable Limit (MDL) is the lowest weight fraction or mass for square centimeter of one element that can be detect in a sample. This quantity can be evaluated knowing the background counts (B_i) under the characteristic peak of the element being analyzed along with the slope (S) of the calibration curve:

$$w_i = \frac{(3\sqrt{B_i})}{dI/dw_i} = \frac{3\sqrt{B_i}}{S} \quad (7)$$

This definition has its foundation on the assumption that the background counts have a Poisson distribution. Therefore, if the counts in the characteristic peak of an element is 3σ larger than the background counts, we can assume the element is detected with a very large probability. Strictly seeking the factor 3 in the equation 7 should be substituted by 3.29 following a more rigorous derivation of the relation for the MDL [28].

As discussed above, using SR for XRF, two model of excitation are available, excitation with monochromatic radiation and excitation with white light. Each mode require specific tradeoffs. Equations 1-5 have been derived for monochromatic radiation. When using white radiation we must weight the equation with the spectrum ($f(E)$) of the SR and integrate over energy:

$$I'_i = \int_{E_k}^{\infty} I_i f(E) dE \quad (8)$$

E_{ph} is the energy of the absorption edge of the element in question. The term $f(E)$ includes also the absorption from the windows and any filters (fig.5). The advantage of using SR are basically two: (1) the inherent polarization of the from the source and (2) the high brilliance.

A synchrotron produces photons that are linearly polarized in the plane of the electron orbit, i.e the plane of the storage ring; the electric field vector lays in this plane (fig.6). The polarization affect the angular distribution of the coherently and incoherently scattered photons in the plane of the storage ring. In particular at ninety degrees the coherent scattering is null and the incoherent is minimized. The advantage of polarization is in the fact that it is possible reduce by two order of magnitude the background from scattered radiation (at least working with a low Z sample). By placing the detector in the plane of the storage ring at 90° to

FIGURE 6 The polarization characteristic of SR are due to the acceleration of the electrons in the plane of the storage ring.

the beam, the intensity of the scattered radiation emitted by the sample decreases.

The high brilliance of the SR makes it easier to construction a microprobe. In fact, in this case the total flux is concentrated in a small cone with a small divergence. Therefore a small area of the beam can be selected with a opportune collimation without a huge decrease of the intensity. The traditional sources are characterized by a large divergence of the beam that make more difficult the collimation of the primary beam. In particular, with the use of optics the beam can focused in a small area of few square micrometers if its intensity is not enough to obtain a satisfactory counting rate [29].

It is evident from equation 1 that the intensity of a characteristic x ray line increases if a monochromatic primary beam approaches the absorption edge of the element being probed. It worth remember that a $E^{-3.5}$ dependence of the photoelectric cross section is well established, therefore if the excitation energy is $E_k + \Delta E$ the fluorescence line intensity decreases by:

$$\frac{I_F(E_k + \Delta E)}{I_F(E_k)} = \left[1 + \frac{\Delta E}{E_k}\right]^{-3.5} \quad (9)$$

The advantage of this enhancement is sensible only when the energy changes are greater than few keV, as is illustrated in fig. 7. Therefore the real advantage of using tuneable radiation is in selectively fluorescing elements. For example chromium in an iron matrix without massive number of iron photons by setting E_0 below the absorption edge of the iron. This technique is somewhat limited since the position of E_0 cannot be too near the edge of the element being selected because the presence of the incoherent band increases the background under the fluorescent line [30].

It is possible to model with some precision the whole performances of a XRF system starting from the fundamental equations

FIGURE 7 Intensity decreases of fluorescent radiation due to the shift of the energy of primary beam toward higher energies.

shown before, this is well known to those people that have developed computer codes that allow the quantitative determination of several elements in a sample, using very few calibration procedures [31,32].

In conclusion, even though the atom being probed cannot distinguish an x ray

from a synchrotron from an x ray from a tube, there are differences in the beams produced by these different sources. Therefore, using SR for XRF is a growing field for several reasons. When compared to XRF with x rays generated from ordinary tubes, SRXRF can have better MDL's, and provides opportunities for microanalysis. The times needed for data acquisition is usually much smaller than the times required for conventional XRF. Because of the intensities, focussing and monochromation become feasible, with monochromatic radiation we can selectively fluoresce elements or can determine chemical states. With the high intensities from focussing mirrors using WD systems with shorter time of acquisition is feasible.

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