PIXE, Particel Induced X-Ray Emission A Concise Review

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PIXE-Particle Induced X-Ray Emission is a multielemental, sensitive and non-destructive method which has been in use in trace elemental analysis since 1970. This review aims to explain the main features of PIXE. References will be given at the end for those that seek more detailed knowledge on the principles and applications of this technique.

Keywords: particle induced X-ray emission, elemental analysis, trace element, ion induced X-ray.

Introduction

PIXE-Particle Induced X-ray Emission is a very sensitive analytical method for trace element analysis based on the production of X-rays by ions accelerated to MeV energies and is in wide use since 1970. The main reason for the growing interest in particle induced X-ray production is that the background is lower in intensity than that encountered by the more conventional methods like X-ray excitation, electron bombardment or excitation by electromagnetic radiation from X-ray tubes or radioisotopes. Although particle induced X-ray emission has been studied since 1958 by Merzbacher and Lewis its broad use as an analytical tool could only be achieved with the development of high resolution semi-conductor detectors which enabled simultaneous, multi-elemental analysis within a few minutes. In 1970 Johansson et.al. detected 10^{-11} gr. using Si(Li) detectors[1]. Since then PIXE has been in use as a sensitive multi-elemental tool for the analysis of trace elements in a wide variety of fields where trace element analysis has been of major importance. These can be listed as follows: Environmental pollution-air pollution and water pollution-biological research, archeological research and material purity studies. A review on the applications of PIXE will be made elsewhere. This paper includes the main features of PIXE. The interested reader is referred to reference[2] for a more detailed review.

A general view of the method will be given first before going into detailed considerations.

General View

A beam of protons (or α-particles, or heavy ions like O^+, Ar^+) are accelerated by an accelerator which is usually a Van der Graaff accelerator and pass through an irradiation chamber (Figure 1). The intensity of the beam is made uniform by means of a diffuser foil or two pairs of electrostatic deflector plates sweeping

the beam in perpendicular directions. The beam is then collimated by a series of collimators. The target area may be a thin target that is a carbon or plastic (polyethylene, Kapton, Mylar) backing material on which the sample is deposited. It may also be a thick target such as organic tissues (teeth, hair) or powder compressed to a pellet. Passing the target the beam reaches the Faraday cup which is connected to a beam integrator so that the current and thus the number of incoming protons can be measured. The X-rays emitted by the sample pass through two thin windows: the target exit and the detector entrance windows respectively. These are usually made of Be-25 μm thick. An absorber of 0.05 m Be can also be added to absorb the unwanted low-energy X-rays. The detector is placed with a 90° angle to the incoming beam and the X-radiation coming from the sample is detected in the Si(Li) detector, processed in the preamplifier and amplifier, stored in the multi-channel analyzer and displayed by a computer program. A typical spectrum of PIXE is seen in Figure 2. At the low energy end of the spectrum there is a cut-off due to the absorption of X-ray by the window of target chamber and detector. Because of this absorption with a standard arrangement there is a lower limit of detectability so only elements down to Aluminium can only be detected accurately. However, using special detectors, e.g. windowless detectors, this range is extended to lighter elements. Spectra showing well defined peaks of B, C, O have been reported[3].
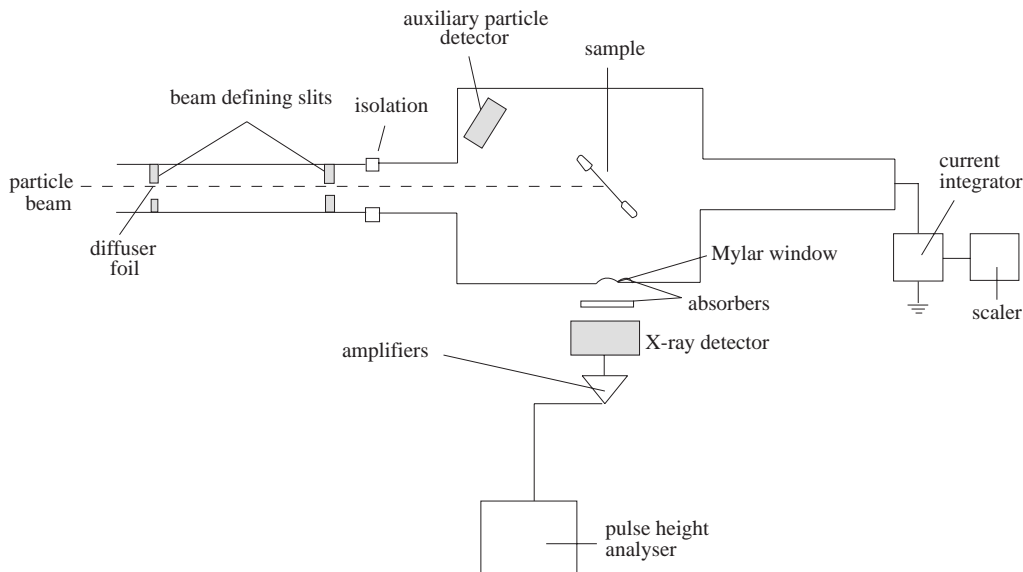

Figure 1. A general view of experimental set-up for PIXE.

      This possibility of covering nearly the entire periodic table in one single run is a major advantage of PIXE.

Interaction Between Accelerated Particle and Target

The interaction between heavy charged particles and target atoms resulting with the removal of at least one inner-shell electron and generation of the characteristic X-rays has been studied since it's discovery by Chadwick in 1921. By "heavy charged" is meant particles heavier than electrons, i.e. protons, alpha particles, O^+, Ar^+ and such. At this point a distinction is made between point charged particles such as protons and alpha on one hand and heavier atoms like O^+, Ar^+, Kr^+, on the other. This is due to the differences in interaction with target atoms. Since, for analytical purposes, only protons and alphas are

important and since heavier ions are used only for special analytical tasks like surface studies a description about the interaction of matter with heavier atoms will be omitted.
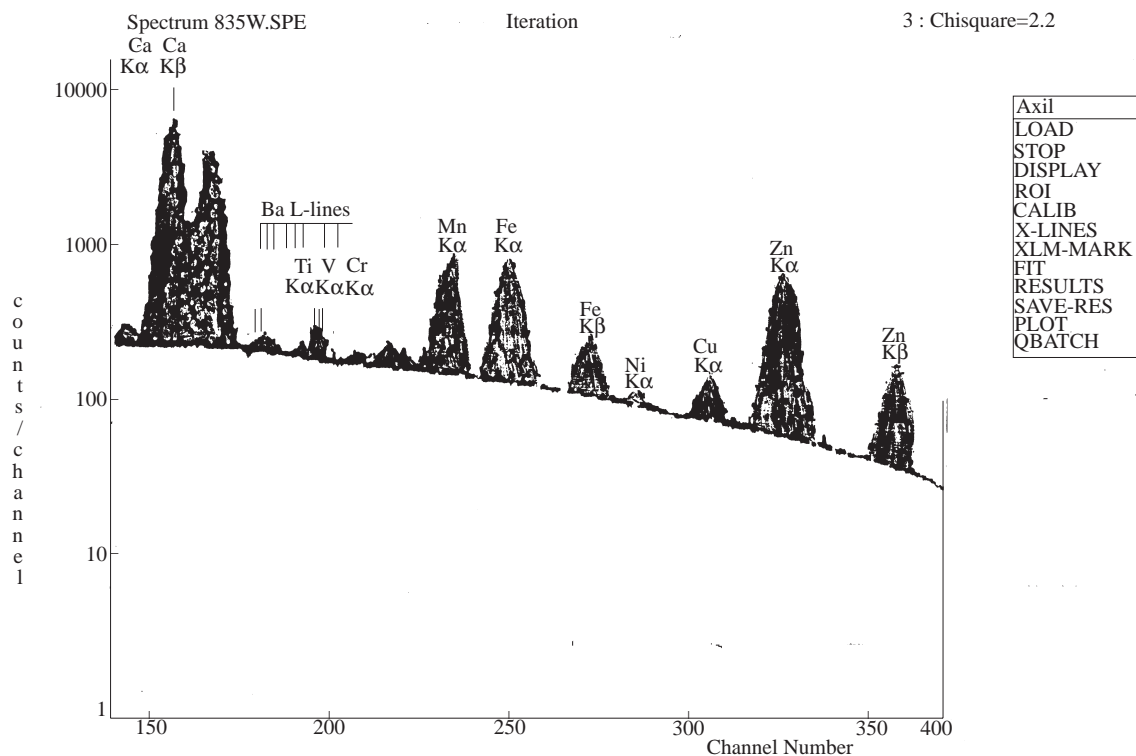

Figure 2. Spectrum of a water sample from Susurluk River[2].

In a spectrum the number of counts in a peak is a measure of the amount of the corresponding element in the sample i.e. it is quantity. In turn, the number of counts that is the intensity of an X-ray line is directly proportional to the ionization cross-section of the shell under consideration. Ionization cross-section is a measure of vacancies i.e. the potential X-ray emission cites produced in the target atom (Fig. 3). Production cross-section gives the effective transitions which end up with X-ray photon emission for which the fluorescence yield has to be taken into consideration. Production cross-section is calculated according to the formula

$$\sigma_p = \sigma_{ion}.w.k, \tag{1}$$

where

$$
\begin{aligned}
\sigma_p &= \text{production cross-section} \\
\sigma_{ion} &= \text{ionization cross-section} \\
w &= \text{fluorescence yield (to take into account Auger effect)} \\
k &= \text{relative line intensity of the transition under consideration,} \\
&\quad \text{e.g. } K\alpha/K\alpha + K\beta.
\end{aligned}
$$

For a precise analytical result the ionization cross-sections for each element at the applied energy must be known.
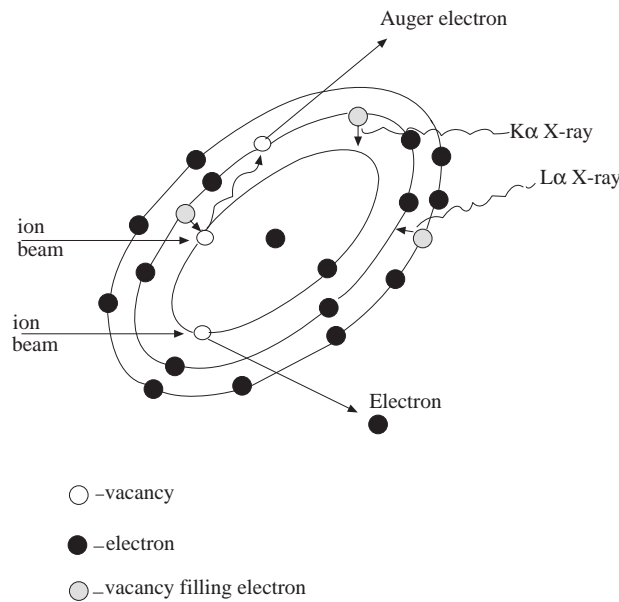
Figure 3. Production of ion induced X-rays ($\alpha \Leftrightarrow \Delta$ n = 1; $\beta \Leftrightarrow \Delta$ n=2.)

The process of vacancy production in the inner shell of the atom and subsequent emission of X-rays by point charged particles is well understood and for heavier ions the main features are known. There are three theoretical descriptions and formulations for the production of inner shell vacancy and calculation of ionization cross-sections. All make the assumption that the production of inner shell vacancy by charged particle impact occurs as a result of Coulombic interaction. That is the electrons are excited by charged particles only via the Coulomb interaction between the projectile nucleus and the target electrons and hence cause Coulomb interaction of K shells[4]. The electron is thus kicked out of the atom, leaving the atom with excess energy and X-rays are generated when an electron from outer orbitals fills the vacancy. The three formulations are:

1. Plane Wave Born Approximation-PWBA-Henneberg 1933, Merzbacher & Lewis 1958[5]

2. Binary Encounter Approximation (Impulse Approximation) Gryzinski 1965, Garcia 1970[5]

3. EPCSSR (modification of PWBA was done by taking into account polarization and binding effects in the perturbed stationary state (PSS) correction for relativistic -R- energy loss-E- and Coulomb deflection-C-hence (ECPSSR)[6,7].

These are high energy formulations in the sense that they are expected to be valid only for incident particle energies that are much larger than the binding energy of the electron[8]. All these approaches can explain to a good approximation the dependence and variation of ionization cross-section with the energy of the incident particles.

However, when the ionization cross-sections estimated by PWBA and BEA approximations were compared with the ionizations obtained experimentally by a great number of authors it was seen that there was 10-30 % deviation. This being no good for quantitative analysis, new approximations were tried. ECPSSR theory, a modification of the PWBA, came out to be a successful theory for predicting K and L shell ionization cross-sections as calculated by Cohen and Harrigan and is in wide use[9]. Johansson in turn formulated a semi-ampirical formula to predict ionization cross-sections to be used in quantitative analysis[10].

Given the energy the ionization cross-section is obtained according to Johansson's graph and the production cross-section which is necessary for quantitative analysis is thus calculated.

In Figure 4 the production cross-sections of K and L X-rays vs. X-ray energies induced by proton bombardment of 2 MeV energy are shown. The curves are calculated by Eq. 1 using Johansson's empirical graph for ionization cross-sections. From the figure it can be seen that for the determination of elements having an atomic number between 13 and 47 (from Al to Ag) the K X-rays and for heavier elements the L X-rays are convenient. The variation of the ionization cross-section with energy of the incident proton must be mentioned at this point. It is seen as a general trend that the production cross-section is a rapidly increasing function of the incident projectile energy. It reaches a maximum for an element and its i'th shell when the velocity of the projectile equals the mean velocity of the electron of the shell under consideration. For higher energies of the projectile the cross-sections slowly decrease. X-ray yield for high X-ray energies i.e. high Z elements (Z > 25) will increase proportional to Ep^4 (where Ep is the projectile energy) but for low X-ray energies the increase is less[12].

An important consequence of the above theories came out to be the scaling property of the ionization cross-sections which is stated as "for equal velocity ions the ionization cross-sections are proportional to Zp^2" (where Zp is the atomic number of the projectile). That is, if the ionization cross-section of an element for proton bombardment of a certain energy is known, the ionization cross-section for other projectiles e.g. an α particle, can be determined without going into detailed calculations.
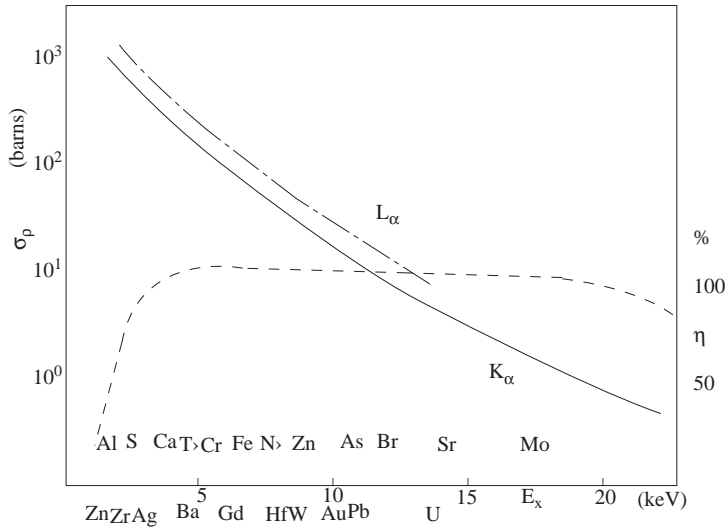
Figure 4. Production cross-section of K and L X-rays induced by 2 MeV protons (the solid and dot and dash lines) and the efficiency curve for a Si (Li) detector v.s. X-ray energies (dashed line). Above the line elements having K X-ray lines, below elements having L X-ray lines are shown[11].

Background

The achievement of a high cross-section for the detection of the spectral line is a necessary condition but is not sufficient for high sensitivity. The characteristic x-ray lines emerge on a continuous spectrum of electromagnetic radiation which we call the background (Fig. 2). It is clear that if this background is high it will prevent the observation of a specific element that limits the sensitivity of detection. This is especially

important for trace element analysis where the element under consideration will produce low count rate due to its small quantity.
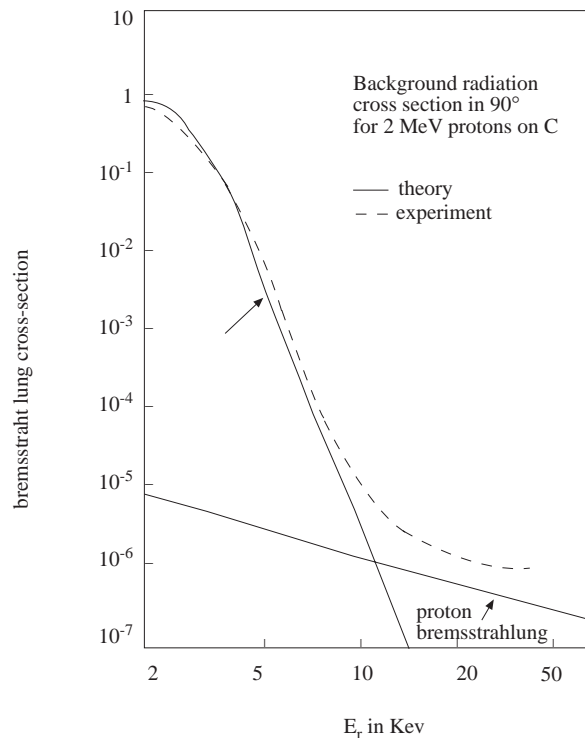
Figure 5. Experimental $(- - - -)$ and theoretical $(—)$ background cross-section for 2 MeV proton on Carbon matrix[14].

Background arises from the impact of the incoming ions with the bulk material of the sample that is the matrix elements. All elements except the element under consideration are considered as the matrix elements.

There are three main processes which contribute to the background (Fig. 5):

1. One is the background formed by the incident particles passing through the matrix where they are deflected by nuclear fields and decelereated. Upon deceleration they emit electromagnetic radiation, bremsstrahlung, which forms the high energy part of the background in the spectrum.

The yield (i.e. cross-section) of this electromagnetic radiation increases for lower projectile energies i.e. decreases as energy of projectile increases and is proportional to

$$d\sigma/dE_r \propto (Zp/Ap - Zm/Am)^2, \tag{2}$$

where p represents the projectile and m the matrix.

It is seen from this proportionality that if the ratio Z/A is the same for the projectile and for the matrix the yield of the bremsstrahlung vanishes. Since for most matrices the charge to mass-ratio is close to 1/2 this contribution vanishes for alpha particles and heavier ions but not for protons. This has been experimentally verified[13].

2. At lower energies the dominant background radiation is bremsstrahlung of secondary electrons. In this case, the mechanism is the following. Projectile hits the matrix elements and electrons are ejected. These electrons are deflected by the electric field of the nuclei and undergo deceleration. This deceleration

causes the emission of electromagnetic radiation that is the formation of bremsstrahlung which constitutes the background in the lower part of the spectrum.

This explanation was based on the fact that this bremsstrahlung decreased rapidly above a certain energy Tm, which is the maximum energy transfer from an ion of mass M and energy Ep to a free electron of mass m.

$$Tm = \frac{4m}{M} \cdot Ep .$$ (3)

The probability of the initial ion ejecting an electron of energy Ee decreases slightly with increasing Ee until Ee = Tm. For higher Ee probability decreases very rapidly (Merzbacher and Lewis, 1958). This has been verified experimentally by Folkmann who made an extensive study on background[14]. It is obvious that if the samples are thin enough the electrons can escape before thay have the chance of radiating most of their kinetic energy as bremsstrahlung in a second collision. But thicknesses needed are impractical.

An important fact about the background radiation that is the bremsstrahlung generated by secondary electrons and the characteristic X-ray lines of trace elements is that in both cases the process is the same. Since the first step for both is the generation of vacancies in electron shells by the incident particle the scaling law applies also for the secondary electron bremsstrahlung. That is due to the scaling property the ratio of the X-ray line to the background will be equal for all particles with the same velocity.

3. A third kind of background arises when the incident particle has a sufficiently high energy to excite the nuclei in the target atoms. When these nuclei are excited they emit gamma radiation which causes Compton scattering in the detector. This phenomeno is the reason for higher background than the theoretically predicted projectile bremsstrahlung in the high energy part of the spectrum.

This type of background strongly depends on matrix composition since some elements like fluorine and sodium have a high cross-section for gamma emission, and some have lower cross-sections. The background increases with increasing ion velocities; and for the same ion velocities heavier ions like the α or ^{16}O have a higher γ radiation cross-sections since they have higher energies. Gamma radiation background becomes an important factor for Z greater than 30 at 3-5 MeV proton energies. Therefore the bombarding energy must be kept as low as possible and protons must be preferred to achieve minimum gamma radiation background. This is actually the main reason why protons of 1-2 MeV energy are the best choice for PIXE[15].

The Spectrum

Having explained the main features of a PIXE spectrum, now a detailed analysis will be made. That is the qualitative, quantitative analysis and the sensitivity of the method. The qualitative analysis of the spectrum with some of the problems that are frequently encountered will be stressed first.

On the x-axis of an X-ray spectrum are the channel numbers corresponding to emitted energies of the elements and on the y-axis the number of counts that correspond to the intensity of the element (Figure 2). The correspondence between the channel number and the emitted X-ray energy is achieved by a calibration chart made by using pure standards. For example, in Figure 2 channel number 260 corresponds to Fe K_{α} which has an energy of 6.4 KeV approximately. But the qualitative analysis of the spectrum is not always so simply straightforward. The often encountered problem is the interference of the X-ray lines of the elements due to the limited resolution of the detector. That is the resolution between two X-ray lines having very close energies is limited by the resolution of the Si(Li) detector. Since the resolving power is fixed, interferences are unavoidable but are solved by other means.

A frequently encountered interference problem occurs when K_{α} of the element Z and K_{β} of the element Z-1 coincide. This is usually seen for lighter elements. Another important interference problem is

encountered for elements for Z greater than 35. The L lines of these elements and K lines of lighter elements coincide (Fig. 2). The same thing is seen for elements in lead region. Their M lines coincide with K lines of light elements. For example for aerosol analysis Ba, Ti and Pb-L and As-K are the most difficult to handle.

To solve the interference problems the best method is to use the relative intensities of the spectral lines of the element sought. The relative intensities of the α/β lines are constant for each element, independent of the mode of excitation and so this ratio is used to determine whether the peak under consideration belongs to one single element or is formed by an overlap of the spectral lines of two elements. This method gives accurate evaluation of the K lines of the light elements. Although the same is valid for L lines the evaluation in this case is more rigorous and only an interference between L lines and K lines can be resolved in this way.

Nowadays the analysis of a spectrum is made with the aid of a computer. The programs which take into consideration the relative intensities of the spectral lines are made of two parts. In one part all probable background effects are considered and on the second part the sum of all the probable characteristic X-rays peaks of all elements are loaded. Given the energy of the projectile and the calibration chart in which the data for the correspondence between the X-ray energy of the elements to channel number is found, the quantitative and qualitative evaluation of the peaks is made. Campbell et.al. made a detailed comparison on the most widely used five spectrum data processing techniques in PIXE[16]. Despite of major differences in their methodologies, which arise from the background description and its combination with the peak model, a remarkably good agreement was found among them. Watjen has summarized the characteristics, the field of applications and the computer configurations of the available PIXE programs at the 4'th International Conference on PIXE at Tallahase[17]. In Figure 6 an example of data processing with Axil program is shown. For quantitative analysis the number of counts in a peak proportional to the amount of the corresponding element in the sample is measured. The evaluation is different for thin and thick targets. Thin targets will be considered first. These are defined as being so thin that the energy loss and therefore the variation of cross-section for X-ray production is negligible.

For thin samples ($< 1\text{mg/cm}^2$) the number of counts detected is given by the formula

$$N_{xi} = Np.A.\Delta\Omega/4\Pi.Ed.C_{abs}.\sigma_p \tag{4}$$

N_{xi} =   number of x-rays coming from i'th shell transtion, e.g. $K\alpha$,

Np =   number of incident particles;

A =   number of atoms of the element per cm^2 of the target;

$\Delta\Omega$ =   solid angle of detector;

Ed =   internal efficiency of detector at the radiation energy under use;

C_{abs} =   Absorption reduction factor for the absorption
of the X-rays from the sample to the detector, sample absorption included;

σ_p =   production cross-section;

In the above equation all variables can be measured:

Np; measured by Faraday cup;

$\Delta\Omega$; solid angle of detector calculated from exact area and distance of silicon detector;

Ed; efficiency of detector at that relevant radiation energy measured by prior calibrations (usually obtained by the manufacturer).

Cabs-absorption of the X-ray in windows and absorbers do not present any problem. But the absorbance of emitted x-rays in the sample itself is a problem especially for low Z X-rays which have lower energies.

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: Region of interest : ch# 138 - 409    3.391-10.067 Kev :
: Chi-square value   : 1.10E+00      in    4 iterations   :
: Last change        : 3.3E-03 %    lamda = 1.E-06        :
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                    CALIBRATION DATA                      :
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: det NOISE (eV) :  194.8 q   50.0 :  144.5 q    2.5     :
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:                       PEAK DATA                         :

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:#     Line   : E(KeV) : rel. int.  : peak area st.dev    :
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:                                                     :
:1 Ca-KA      : 3.691  : 1.00000    : 36908. q 198.       :
:2 Ca-KB      : 4.013  : 1.00000    : 19474. q 147.       :
:3 Ti-K       : 4.509  : .76110     :    25. q  41.       :
:             : 4.932  : .23890     :     8. q  13.       :
: 4 V-K       : 4.950  : .79399     :   100. q  40.       :
:             : 5.427  : .20601     :    26. q  10.       :
: 5 Cr-K      : 5.412  : .82129     :   116. q  32.       :
:             : 5.947  : .17871     :    25. q   7.       :
: 6 Mn-K      : 5.895  : .83212     :   171. q  32.       :
:             : 6.491  : .16780     :    35. q   6.       :
: 7 Fe-K      : 6.399  : .84368     :  2314. q  53.       :
:             : 7.058  : .15632     :   429. q  10.       :
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Figure 6. Results of peak evaluation by Axil Program[2]

For homogeneous and thin targets a correction can be made by a straightforward calculation with standards. Since all above quantities are either known or can be calculated the only unknowns are A and N_x, N_x is measured experimentally and so A, i.e. the number of atoms of the element/cm^2, is calculated. The amount of the trace element will be thus found.

The analysis of thick samples[18] has the advantage of simplicity since no tedious target preparation is needed as is for thin targets. The risk of contamination of the sample is also minimized. Actually, in some

cases, thick target analysis is unavoidable because it is impossible to prepare thin targets as is the case for biological tissues like bone, teeth, hair, organic tissues, and metallurgical samples.

Although there are advantages coming from the simplicity of target preparation, there are several disadvantages of using thick targets coming from the difficulty of quantitative determination of elements in a thick target. This is especially so when the targets are non-homogeneous. Most of the X-rays generate from the top part of the target, and if a trace element is accumulated on the top, the number of counts may be misleading for the whole sample.

In the quantitative determination of thick targets there are two important factors. One is the slowing down of the bombarding particles and therefore a decrease in their energy. This causes a decrease in X-ray production. The second is that the emitted x-rays are absorbed in the target itself before reaching the detector. Both of these factors cause the number of counts to be lower than the actual number of counts the element under consideration can generate. If the substance is homogeneous elaborate calculations can be done taking these factors into consideration. But the usual widespread practice is to use internal standard[19]. In this case, the sample is doped with a suitable chemical compound of known concentration and the number of counts of the trace element are normalized with those of the internal standard. With the use of internal standards samples that are thick by nature or those that cannot be made into thin targets like the above mentioned (e.g. hair, bone, teeth) can be routinely analyzed. An important note here is that since the energy of the particle beam is deposited in the sample this can cause overheating which then causes deterioration of the sample. This must be predicted and heat conducting materials added if necessary.

Sensitivity

The overall sensitivity of the PIXE method is determined by the production cross-section, the magnitude of the background and the efficiency of the detector system. It will suffice in this context to emphasize the main features which will be enough to describe the efficiency of the PIXE method.

There are several ways of defining the sensitivity of an analytical method. In this case the problem is to find small amounts of trace elements in a certain matrix. Therefore we define sensitivity as the minimum detectable concentration (M.D.C.).

Trace elements are always contained in a matrix. And as explained before a background is inevitably formed. It is this background that mainly sets a limit to the sensitivity of the method. Since the background depends on composition of the matrix it is impossible to give a general simple expression for sensitivity[20].

Nevertheless, some general criteria have been stated to determine sensitivity. Also, the factors that minimize background and therefore increase sensitivity are known. First of all the characteristic X-ray lines must rise above the background in a statistically significant way. It is generally accepted that the characteristic peaks must satisfy the equation:

$$Np > 3\sqrt{Nb}, \tag{5}$$

where Np is counts of peak, Nb is number of counts in the background under the peak in a defined interval[21]. With this criterion the minimum measurable amount of a trace element in a certain matrix can be calculated from the available background data, the cross-section of the trace element and the experimental conditions. Folkman et.al. calculated the minimum detection limits (Fig. 7) for proton, α and ^{16}O induced X-rays[12,14,15].
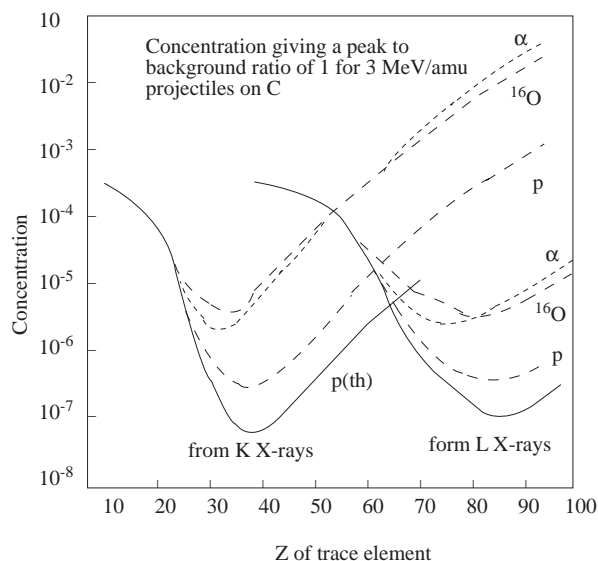
Figure 7. Minimum detectable concentration as a function of atomic number for protons, alpha, ^{16}O [15].
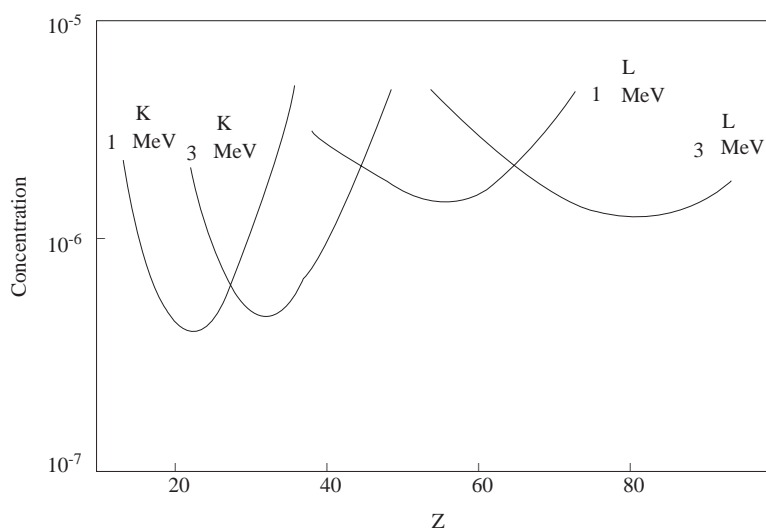
Figure 8. Minimum detectable concentration as a function of atomic number for protons of 1 and 3 MeV [10].

When the below values are taken one gets: Ed = 150 eV at 5.9 keV, Ω = 0.003 × 4psr, collected charge j = 10 μC and target thickness t = 0.1 mg/cm^2 which are just suitable for a rough routine analysis the variation of minimum detectable concentration with Z for proton energies 1 and 3 MeV are found to be as in the Fig. 8.

It can be seen that all curves have a minimum detectable concentration that manifests as maximum sensitivity in a certain Z range. For light elements this minimum detectable concentration increases, that is, sensitivity decreases due to the decrease in fluorescence yield. In contrast to heavier elements this decrease in sensitivity is due to the decrease in X-ray cross-section while the background is relatively constant. The position of maximum sensitivity i.e. minimum detectable concentration depends on energy, thus according to the range of interest the energy of proton can be adjusted to have the highest sensitivity.

For elements of Z > 40 intensity of K X-ray lines is too small, but L X-ray lines can be used for the determination of these elements. Therefore, by using both K- and L X-ray lines, a minimum detectable

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concentration of about 10^{-6} can be achieved over nearly the whole periodic table.

Considering the effect of the matrix on sensitivity for a fixed proton energy it was found that it was advantageous to have light elements as a matrix. This is because Z increases proton bremsstrahlung as well as bremsstrahlung due to secondary electrons increase. Since, for biological samples, carbon is the main matrix element, this becomes an advantage in the analysis of biological samples[12].

So far sensitivity of the method with proton excitation has mostly been discussed. It will be interesting to see whether higher sensitivities can be obtained with projectiles heavier than protons like α or Oxygen. The same sensitivity, i.e. the same peak to background ratio, will be obtained for low energy X-ray values (low Z) since both peak and bremsstrhlung have the same initial process and Zp^2 dependence due to scaling law. However, for high energy X-rays (high Z), even if the projectile bremsstrahlung goes to zero because the $(Zp/Ap-Zm/Am)^2$ factor goes to zero, the strong Compton γ-ray background drastically decreases the sensitivity limits compared to protons.

All these considerations show that the best choice of excitation are the 1-2 MeV protons.

All the above sensitivity limits can be increased by adjusting the experimental parameter's, taking into account the background and cross section. For a certain matrix and energy the sensitivity scales according to the following experimental parameters:

$$\Delta E^{-1/2}(\Omega.j.t)^{1/2},$$

where ΔE is the energy resolution of the detector, j is the collected charge and t is the target thickness. A table showing each parameter's effect will be helpful to understand the variation of minimum detectable concentration with these parameters (Table 1).

Naturally these parameters cannot be randomly decreased or increased since other factors will then have to be considered. For example, when target thickness increases sensitivity increases but then the problem of absorption of X-rays and decrease in X-ray production cross-section will arise so optimization of the system is needed.

Before going into the optimization of the system an example will be given for the calculation of the minimum detectable amount reached within certain sensitivity limits. The minimum detectable concentration (m.d.c.) must be known for the calculation of the minimum detectable amount. For example with a target thickness of 10^{-4} g/cm^2 and a beam area of 1 cm^2 a minimum detectable concentration of 10^{-6} corresponds to 10^{-10} grams. But one can without any difficulty use a target thickness of 2×10^{-5} and a beam area of 1 mm^2 and push the m.d.c to 10^{-7} and this will correspond to 2×10^{-14} gr. By making beam diameter smaller amounts of 5×10^{-17} gr. have been estimated.

Being able to measure such small amounts of trace elements with very small amounts of sample material is a big advantage in biological and environmental studies.

Optimization of the Method

Actually the optimization of the method comes out of the foregoing discussions, so only the main points will be stressed. It must first be stated that the optimum conditions are determined by the samples to be analyzed, so there is no general optimum condition valid for all cases. Instead the analyst must choose its own optimum according to it's needs. Nevertheless for routine analysis there are some factors of general validity.

1. First of all, protons seem to be the best choice for the bombarding particle compared to α and heavier ions. This is because even if, at the same velocity, the ionization cross-section of α particles is

higher the γ radiation background they generate decreases their overall sensitivity. This effect is much more pronounced for heavier particles. Another problem with α particles is that they cause heating and deterioration of the sample at high energies and if their energy is decreased the cross-section of ionization also decreases. However, when a high sensitivity is not required protons and α particles are approximately equivalent.

2. When adjusting the bombarding energy it must be kept in mind that at proton energies 3-5 MeV and for Z > 30 the γ radiation background becomes important, reducing the sensitivity. So energy must be kept as low as possible without causing a decrease in ionization cross-section. For each part of the periodic table there exists a best energy for ionization. But if in a single run a great part of the periodic table is sought an optimum energy has to be found. If the trace element analysis is made for biological and environmental samples which are Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Rb, Zr, Mo, Cd, Hg or Pb the main interest is concentrated in two regions. Figure 9 shows variation of sensitivity as a function of bombarding energy and Z.
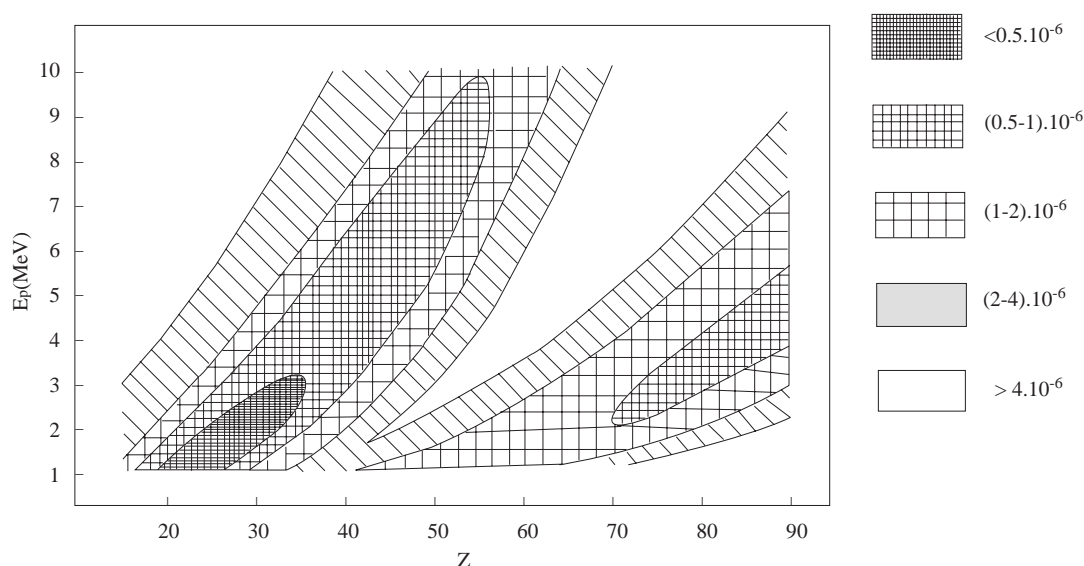
Figure 9. Minimum detectable concentration as a function of atomic number and bombarding energy[10].

It is clear that the optimum energy for the above regions is about 2 MeV. This is a fortunate phenomena from several points of view. First of all, both regions of interest can be analyzed with the same bombarding energy. Secondly, the γ-ray background can be minimized because of lower energy and, thirdly, from practical point of view it is easier to find small accelerators that can produce 2 MeV protons for lower prices, thus enabling the usage of PIXE routinely.

3. The optimization of the experimental conditions can be made remembering that minimum detectable concentration scales as $\Delta E^{1/2}(\Omega jt)^{-1/2}$ for the same energy as in Table 1.

Comparison with Other Spectrometric Methods

Having made a general view of the properties and sensitivity of particle induced X-ray emission spectroscopy it is useful to make a short comparison with other commonly used spectroscopic methods so that according to the purpose a correct choice of the analytical method can be made.

Table 1. [10−20]

Energy	Parameter	Comment
Experimental conditions at any energy	$(E)^{1/2}$-energy resolution of detector increases	-limited by the available detector resolution
	$(\Omega)^{1/2}$-solid angle of detector increases	-can be achieved by closer spacing to beam, but possible damage in detector due to neutrons and scattered charged particles.
	$(j)^{1/2}$-collected charge increases	-by longer irradiation times (increased cost), and high beam current but then possible target damage
	$(t)^{1/2}$-thickness increase	-decrease in ionization cross-section due to stopping power, and attenuation of x-rays.
at a certain energy	σ_x-trace element cross-section increase	
	σ_B-background cross-section decrease.	

The most commonly used X-ray emission spectroscopic methods are electron excited X-ray emission and photon excited (γ or X-ray) X-ray emission spectroscopy which is often called X-ray fluorescence spectroscopy.

Electron excitation is mainly used in connection with electron microscopes or scanning electron microscopes. Electron excitation and generation of X-rays shows many similarities with proton and heavier ion X-ray generation since they are also charged particles. Typical electron projectile energies are 20-50 KeV. These electron projectile energies create the same cross-section for vacancy production as 2-4 MeV protons. In this respect they are much alike. And they have the advantage of being more easily focused so that a very fine structural determination of very small samples (e.g. cell structure) can be made. But they have a major disadvantage that limits their use in trace element analysis. This is the very high background formed by bremsstrahlung radiation produced by deceleration of electrons.

Intensity of bremsstrahlung radiation depends on

$$\frac{z^2 Z^2}{m^2} \tag{6}$$

where z is the charge of the projectile, Z is the charge of the target atom and m is the mass of projectile.

Since the electron/proton mass ratio is 1/1850 it is clear that the bremsstrahlung arising from proton bombardment is much lower. The bremsstrahlung arising from electron bombardment is about 3 to 4 orders of magnitude higher than the proton bremsstrahlung.

So an electron microscope cannot detect trace elements but only the main constituents of a sample and, since the samples are very thin and a fine focusing is possible, absolute amounts up to 10^{-16} gr of the main constituents can be detected accurately.

Excitation with X-rays, that is, the X-ray fluorescence method is one of the most widespread methods for trace element analysis. Many workers have made detailed analysis to compare the efficiency of X-ray fluorescence and PIXE[22]. X-rays (or γ-rays) used as excitation source are produced either by radioisotope sources or are the continium radiation produced by X-ray tube. The production of characteristic X-ray lines by X-ray excitation is a different phenomena than particle bombardment excitation since it involves the absorbance of X-rays. It has been shown that minimum detectable concentration is in the order of about 10^{-6} ppm and this is the same as the minimum detectable concentration which can be obtained by PIXE. But PIXE has a major advantage. For X-ray excitation the analyzed material is of the order of grams or decigrams so the detectable amounts are of 10^{-7} to 10^{-8} grams. The possibility of analyzing very small samples is a major advantage of PIXE. Remembering that minimum detectable concentration can be pushed down to 10^{-7} ppm and that samples on microgram scale can be measured a minimum detectable amount of 10^{-12} gr is easily achieved in PIXE analysis. These values indicate that PIXE has a greater sensitivity than X-ray fluorescence method and therefore present a superior analytical method especially for air pollution studies, biological tissue analysis, semi-conducting materials etc. On the other hand, X-ray fluorescence has its advantages. One of the most important being the simplicity of the apparatus.

Some of the other most widespread analytical methods used in elemental analysis are Atomic Absorption Spectroscopy, Inductively Coupled Plasma and Neutron Activation Analysis[23,24]. Atomic Absorption can reach very low detection limits (0.001 ppm to 0.02 ppm for a great number of elements); however, any element that is not precharacterized cannot be determined. ICP, a kind of emission spectroscopy, is also a very sensitive method (sensitivities in ppb range) but it has the disadvantage that samples must be converted into aerosol form to be analyzed. Neutron Activation Analysis is the most sensitive method in elemental analysis. However the sensitivities of NAA have a large range from $10^{-5} \mu$g for Mn to e.g. 50 μg for Fe as the minimum detectable concentration. Another important disadvantage is the time required for the decay of the radioisotope, which maybe as long as days.

PIXE overcomes these disadvantages in that it is multi-elemental, tedious sample preparation is not needed, results can be obtained in a few minutes, it is non-destructive i.e. very small amounts of sample is sufficient to detect easily e.g. 10^{-12} gr. of trace element. Taking into consideration its advantages the Louvre Museum has established a PIXE facility to determine forgery of the pictures measuring the Ti content by sampling very small amounts.

At this point it must be stressed that those methods do not compete but complement each other and they must be chosen according to the researcher's purpose.

Lastly, using PIXE as an analytical method is not so costly as it may seem. The need of an accelerator might make one think so. On the contrary, due to their low energy, the accelerators are not used for physics research, yet are well suited for PIXE. The 4 MeV Van der Graft Accelerator at the Bohr Institute at

Copenhagen is used exclusively for PIXE work. Cahill and co-workers estimated a 5$ cost per sample for 700 runs a day with the Davis cyclotron, most of the cost going into labor and handling[25].

Since the optimum energy is about 2 MeV a small electrostatic accelerator can be bought for this purpose and this will cost only about 200.000$. If it is amortized over a period of ten years the capital cost per year is about $30.000 and if it is used full time it can analyze 50.000 samples a year so this means that the cost per sample will be $0.5.

Considering the details of the principles and the methods used with PIXE, this has been only a short review. Those that are interested and would like more knowledge on PIXE are referred to the Ph.D. thesis of the author of this paper in which detailed examples on qualitative and quantitative calculations can be found, papers given in references[2,10,12], the book on PIXE written by the noted Johansson and Campbell[26,27] and the PIXE conferences held every three years published in Nuclear Instruments and Methods (...1987, 1990, 1993) in which applications of the PIXE method can be found. A paper which will summarize these applications is being prepared by the author of this paper.

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