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Particle-induced X-ray Emission: A Useful Analytical Method

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In 1970, it was shown experimentally by Johansson *et al.*¹ that the excitation of atoms by charged particles, *e.g.*, protons, and the subsequent detection of the induced X-rays by an energy-dispersive detector constitutes a non-destructive multi-elemental method with low detection limits and several other properties desirable in an analytical method. Since then, many investigations have been performed and the method, known as particle-induced X-ray emission (PIXE), has been developed further. The development of suitable methods of pre-treating samples for PIXE analysis has also been intensively pursued. In the Proceedings of the International Conference of Particle-induced X-ray Emission,² the method and its applications are thoroughly reviewed. Two reviews have also recently been published.^{3,4}

In this summary, the principles and properties of PIXE are discussed. Possible areas of application are briefly discussed, and limits of detection of elements in blood plasma are considered.

Principles of PIXE

When a beam of protons, alpha-particles or other heavy ions bombards a sample, X-rays are emitted, the energy of which is characteristic of the elements from which they originate. The number of X-rays of a certain energy emitted is proportional to the mass of the corresponding element in the sample.

In addition to the characteristic X-rays, a continuous X-ray spectrum is also created, mostly due to bremsstrahlung from decelerating electrons, which have been accelerated by the bombarding particles. However, in comparison with electron excitation and X-ray excitation, the continuous components are of low intensity in particle excitation.

By using an energy-dispersive X-ray detector, *e.g.*, a lithium-drifted silicon detector, a multi-element method for simultaneously identifying and assaying the elements in the sample is obtained. From the detector a pulse-height spectrum is obtained from which the elements present in the sample and their masses can be calculated, preferably with a computer.

K X-rays are normally used for measuring elements lighter than barium and L X-rays for those which are heavier. The simultaneous occurrence of both light and heavy elements may cause problems with interferences, but often a good computer program is able to detect small differences in energy and provide information even about minor peaks. Although their efficiencies are low, wavelength-dispersive detectors can also be used to resolve interferences, as they have a superior energy resolution in the low-energy end of the X-ray spectrum.

Properties of PIXE

In particle excitation, the probability per particle of inducing characteristic X-rays is high and, in most instances, there is no problem in obtaining adequate intensities of the particles. Also, as mentioned above, the non-informative radiation components are relatively small. Thus, the detection limits are low and are normally set by the data-taking capacity of the detection system. A useful feature of the detection limits is that they vary smoothly and not very rapidly with the atomic number of the element and particle energy. Absorbers

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inserted between the sample and the detector attenuate mostly low-energy X-rays, giving an opportunity of increasing the intensity of the bombarding particles without increasing the total intensity of the X-rays reaching the detector. Thus, it is possible to optimise the sensitivity to suit the particular kind of information the analyst wants. Another method of optimisation is to change the particle energy, because the relative excitation probabilities vary with incident particle energy.

For an element with a low atomic number, the sensitivity decreases owing to absorption in the materials between the sample and the detector. Also, absorption of these low-energy X-rays in the sample itself requires a correction that may be uncertain. Thus, for most applications, the PIXE method is quantitative only for elements heavier than phosphorus.

In combination with other methods, PIXE offers a number of unique possibilities of obtaining information about elements with low atomic numbers. Thus, Malmqvist *et al.*⁵ reported the possibility of using a nuclear method for simultaneous measurements on fluorine. Another means of obtaining quantitative information about most low atomic number elements is to detect the back-scattered particles.

Mass calibration is easy owing to the known behaviour of the physical parameters involved in PIXE analysis. Once the calibration has been made, only rapid periodic control runs with a suitable standard have to be performed in order to check that no changes in the experimental arrangement have occurred. For routine analysis, the accuracy is about 10% for elements well above their limits of detection.

The most common types of sample analysed by PIXE are thin, solid samples. By "thin" in this context, we mean samples in which both the slowing down of the bombarding particles and the attenuation of the characteristic X-rays are negligible. Of course, this definition of "thin" depends critically on which particles are used, their energies and which X-rays are detected. Usually, however, samples thinner than about 1 mg cm^{-2} can be considered to be thin.

A considerable advantage of PIXE is its low detection limits in very small samples ($1 \mu\text{g}$ - 1 mg). In a routine analysis lasting 1-4 min, the limit of detection varies between 0.1 and 10 ng.

Often, it is either impractical or impossible to obtain representative thin samples. If sufficient material is available, a homogeneous pellet with a smooth surface can be prepared and analysed. It is just the first few milligrams per square centimetre of the surface layer that contribute to the yield of X-rays.

As such a small volume is analysed, the concentration detection limits are moderate and are typically in the range from 1 to 100 p.p.m.

Thus, when PIXE is used for thick samples, it is because of its speed, the straightforward pre-treatment possible and its multi-element capability rather than because of its limits of detection. Also, it may be pointed out that it is often of minor advantage to be able to prepare thin samples, if it is easier or more convenient to make homogeneous pellets.

Arrangements for PIXE in Lund

At the University of Lund, a 3-MV tandem Pelletron is used, protons up to 6 MeV being available. In the routine analyses performed, 2.5-MeV protons are used and the beam is made homogeneous by letting it pass through a $6 \mu\text{m}$ thick aluminium foil. The number of protons striking the sample is measured by a charge integrator coupled to the experimental chamber. An electron suppressor at -50 V is used to prevent low-energy electrons passing between the Pelletron transport tube and the irradiation chamber. To avoid charging of the sample, an electron gun is used for decharging.

For routine analyses, an automatic sample changer with a capacity of 40 samples is available. Two standards are usually loaded in each sample tray, one at the beginning and the other at the end.

Applications

In the characterisation of air pollution, size-distribution information is often essential. A sorting tool often used is the cascade impactor. For both convenience and the impactation of

small particles, it is feasible to use small impactors. The function of impactors at high loadings is, however, questionable owing to bounce-off effects. Thus, the samples obtained are usually very small and this is a case where PIXE is a very favourable method. Many PIXE investigations of atmospheric air pollution have been carried out, and the number of samples to be analysed in such investigations is usually very high. With the PIXE method, it has become feasible to perform large-scale investigations with good size resolution and/or good time resolution.

Filter samples of airborne particulates are also suitable in many instances for PIXE analysis owing to its speed and multi-element capability.

The use of PIXE for trace-element analysis in water is of increasing interest and different methods of obtaining suitable samples have been used. By employing evaporation^{6,7} or chelating techniques,^{8,9} limits of detection in the parts per billion range for elements of medium atomic number are obtained.

For samples of biological material, pre-treatment is usually performed, *e.g.*, wet ashing, low-temperature ashing, freeze-drying or grinding have been employed both at Lund and elsewhere.¹⁰ For plasma samples, we have found freeze-drying to be suitable and Fig. 1 shows the lower limits of detection. Table I lists the elements that normally occur in plasma above and at the limits of detection. Owing to similarities in the compositions of biological material, the diagram is also valid for other biological material if dry-mass measuring is used. Tooth and bone samples can be bombarded directly but damage due to heating sometimes constitutes a problem. For this and other reasons, some laboratories have constructed facilities for optional analysis in air or a gas at atmospheric pressure.

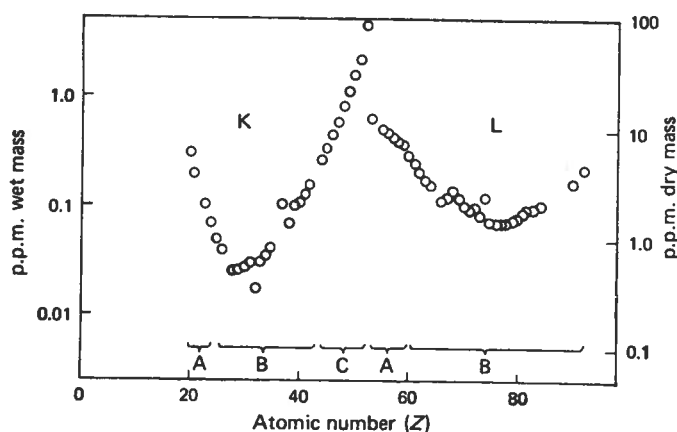


Fig. 1. Experimental detection limits for elements in plasma (with atomic number between 20 and 92) calculated as those concentrations which give a peak three times the square root of the number of pulses in the background in the peak region. Due to interferences, β -peaks have been used in some instances and, in addition, some elements have been excluded (those with atomic numbers $Z = 27, 36, 43, 54, 69, 72, 85-89$ and 91). The limits of detection are calculated for an analysis time of 5 min and a count rate of $2\,000\text{ counts s}^{-1}$ using three different absorbers. About the same limits of detection could be obtained in a single analysis by using absorbers with three different foil thicknesses. Absorbers: A, $50\ \mu\text{m}$; B, $920\ \mu\text{m}$; and C, $2\,000\ \mu\text{m}$.

Although further development of PIXE can be foreseen, *e.g.*, especially concerning the speed of analysis and an extension of the range of elements analysed by either using more than one detector or using complementary methods simultaneously, we consider that major progress, at least in the near future, will be made in the pre-treatment of samples.

TABLE I
ELEMENTS IN BLOOD PLASMA WITH NORMAL LEVELS ABOVE OR AROUND THE
DETECTION LIMITS

Elements above detection limit																					
Level, p.p.m. wet mass ¹¹	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">P</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">S</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Cl</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">K</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Ca</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Fe</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Cu</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Zn</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Br</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Rb</td> </tr> <tr> <td style="padding: 2px;">132</td> <td style="padding: 2px;">1 220</td> <td style="padding: 2px;">3 950</td> <td style="padding: 2px;">170</td> <td style="padding: 2px;">99</td> <td style="padding: 2px;">1.14</td> <td style="padding: 2px;">1.12</td> <td style="padding: 2px;">1.6</td> <td style="padding: 2px;">3.9</td> <td style="padding: 2px;">1.2</td> </tr> </table>	P	S	Cl	K	Ca	Fe	Cu	Zn	Br	Rb	132	1 220	3 950	170	99	1.14	1.12	1.6	3.9	1.2
P	S	Cl	K	Ca	Fe	Cu	Zn	Br	Rb												
132	1 220	3 950	170	99	1.14	1.12	1.6	3.9	1.2												
Elements around detection limit																					
Level, p.p.m. wet mass ¹¹	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Ti</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Ni</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Ge</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">As</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Se</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Pt</td> <td style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 2px;">Pb</td> </tr> <tr> <td style="padding: 2px;"><0.04</td> <td style="padding: 2px;">0.042</td> <td style="padding: 2px;"><0.03</td> <td style="padding: 2px;">0.040</td> <td style="padding: 2px;">0.11</td> <td style="padding: 2px;"><0.04</td> <td style="padding: 2px;">0.043</td> </tr> </table>	Ti	Ni	Ge	As	Se	Pt	Pb	<0.04	0.042	<0.03	0.040	0.11	<0.04	0.043						
Ti	Ni	Ge	As	Se	Pt	Pb															
<0.04	0.042	<0.03	0.040	0.11	<0.04	0.043															

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