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HAIR ANALYSIS USING PIXE

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内容摘要：

质子荧光和质子反散射分析单[illegible]头发中痕量元素的含量及其沿着头发或是在头发的某个横断面上的分布情况。

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Abstract

A simple and new technique for examining single hair strands to obtain linear mass densities, longitudinal profiles and transverse distributions of each trace element is described. It is primarily based upon the PIXE technique, in combination with proton back-scattering. The three main components of this technique are: 1) An accurate way of using an interpolation method to evaluate the magnitude of the correction factor accounting for the proton energy loss and X-ray absorption in the bulk of the hair is formulated; 2) A simple method to qualitatively determine the transverse distribution of each trace element in a hair is introduced and proved to be effective; 3) Proton back-scattering is proved to be capable of providing an ideal linear measure of the geometric hair diameter, one of the most important parameters in quantifying the results of PIXE measurements in mass concentrations. Using the technique, a PIXE system designed and constructed for routine longitudinal scanning of single hair strands is also described.

Key words
Particle Induced X-ray Emission, PIXE, hair, element analysis, elemental distribution, proton back-scattering

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To the memory of my father

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by

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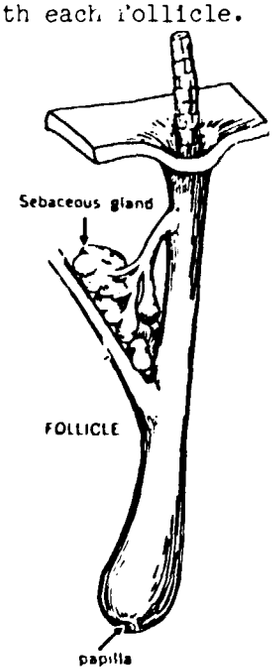
SUMMARY

1. Introduction

Because trace elements play very important roles in human metabolism and nutrition, it is of great concern to find some simple method of examining an individual's trace element status. Analysis of faeces and urine is often of limited value as they carry information which only reflects the intake on a short term basis, and blood has restricted use because the haemostatic mechanisms operate to suppress variations of concentrations of many trace elements. Elemental concentrations along a single hair strand often constitute a chronologic recording of important aspects of the trace elemental status of the body over a long period of time. Furthermore, hair is a kind of biopsy material which can be easily obtained and transported.

A human scalp hair arises in a tubular hair follicle in the epidermis, which extends down into the dermis, where it is surrounded by connective tissue. The active follicle has an expansion with a concavity in its bottom occupied by a connective tissue papilla. The cells of the papilla form the hair root which develops into the hair shaft. The free end of the shaft protrudes beyond the structure of the skin. One or more sebaceous glands are associated with each follicle. They discharge their secretory product into the upper portion of the follicular canal. When the hair is in a phase of growth (anagen phase), the cells around the papilla differentiate into several types. In certain types of coarse hairs the central matrix cells on top of the convexity of the papilla develop into the medulla of the hair shaft. The next concentric layer of matrix cells keratinizes and develops into the cortex of the hair, the main constituent of the shaft. Its cells carry most of the pigment of the hair. Peripheral to the matrix cells of the cortex lie those of the cuticle of the hair. These cells are the most heavily keratinized and act as a protective layer for the hair. These three layers of cellular components all undergo keratinization in the

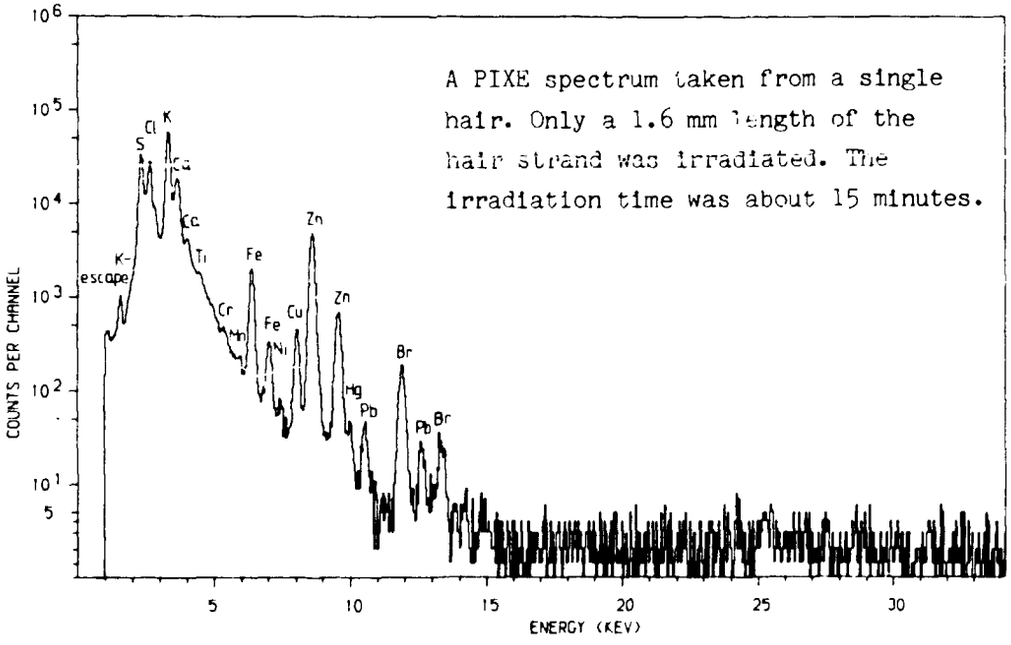


so-called keratogenous zone of the follicle, immediately above the dome of the dermal papilla, and form the solid hair shaft. When using hair as a monitor of trace elements in the body, it is assumed that the trace elements are incorporated into the hair during the formation of the various cellular components in proportion to their levels in other parts of the body, e.g. body fluids and tissues.

Different methods for trace elemental analysis have been applied to single hair strands. Techniques such as neutron activation analysis, atomic absorption spectroscopy and X-ray fluorescence analysis have been used extensively. However, the results have not been very encouraging. The problems are two fold: first, the absolute amount of a trace element in a hair strand is small, which means not only that the method used for hair analysis should be very sensitive, but also that contamination during sample preparation can present very serious problems; second, the concentration of a trace element in a hair strand is a function of many factors, and it is not clear to what extent the measured trace element level reflects internal conditions (nutrition, disease and genetic effect etc.), and to what extent it reflects environmental effects (air, water and soil etc.). Therefore, it is necessary to find a method which can not only accurately quantify the small amounts of trace elements in a hair strand, but also, to a certain extent, assay its endogenous or exogenous origin.

2. The PIXE method

The very promising features of combining X-ray excitation by protons with X-ray detection using a Si(Li) detector for elemental analysis were first described and experimentally demonstrated by Johansson, Akselsson and Johansson in 1970. The work was promptly taken up by many nuclear physicists in other accelerator laboratories, and a rapid development of the technique has followed. Three international conferences on particle induced X-ray emission (PIXE) and its analytical applications have been organized. It is now quite clear that the introduction of PIXE as an analytical tool has created many new possibilities in various different research disciplines (medicine, biology, aerosol science and environmental technology, forensic science, archaeology etc.), of which the work described in this thesis is intended to be an example.



The principle of PIXE analysis may be simply explained as follows: a beam of charged particles (protons, α-particles or other ions) with an energy in the region of 1-5 MeV/u from an accelerator (electrostatic accelerator, cyclotron or an ion accelerator of other type) is used to irradiate a sample, in order to create vacancies in the inner electronic shells of the atoms present in the sample. When the vacancies are filled by electrons from outer shells, X-rays with energies characteristic of each element in the sample will be emitted with certain probabilities. The number of atoms of each element present in the sample can thus be determined by measuring both the energies and intensities of the characteristic X-rays emitted using a solid state detector.

PIXE is a non-destructive, multi-elemental method for fast microanalysis. Ten to thirty elements, heavier than aluminium, can be quantitatively determined in a normal single irradiation. Furthermore, the detection of nuclear reaction products (elastically scattered charged particles, γ-rays etc) can be carried out simultaneously with

PIXE analysis. This extends the analytical capability to many lighter elements (Al, Na, F, C, Be etc.). The mass detection limit for a small sample is low, typically between 0.1 and 10 ng. The speed of performing a PIXE analysis is high. A complete multi-elemental analysis of a specimen can be carried out within minutes.

Papers discussing the application of PIXE to hair analysis began to appear in the literature in the early 1970's. Three different approaches have been used in PIXE analysis of hair samples. The first approach is to use physical or chemical methods to break down the structure of the hair, then form the material into a homogenized thin specimen, and then analyse it using the PIXE method. This approach has two disadvantages. First, all the information relating to the elemental distribution along a hair strand and over its transverse cross section is lost. Second, the contamination in the preparation of the sample often presents serious problems. The second approach is to expose a hair directly to a normal millimetre proton beam for either the analysis of a single piece of hair or a longitudinal scan of the whole hair. The main problem with such an approach is that a hair fibre is a complicated biopsy material, and it is not simple to derive the mass concentrations of the trace elements in the hair from the measured PIXE data. The third approach is to use a proton microprobe to make a PIXE scan across the diameter of a hair. This approach has been used in several laboratories to investigate how various trace elements have been introduced into the hair. However, it takes hours to make such a scan, and the preparation of a hair cross section specimen is also a very tedious task. Hence, it is not very practical to use a proton microprobe to examine single hair strands on a routine basis. This thesis focuses on the second approach offering a procedure for quantification of trace elemental concentrations in single hair strands, that is useful for routine investigations.

3. Thesis

A simple and new technique for examining single hair strands to obtain linear mass densities, longitudinal profiles and transverse distributions of each trace element is described in this thesis. It is primarily based upon the PIXE technique, in combination with proton back-scattering. The three main components of this technique are: 1) An accurate way of using an interpolation method to evaluate the

magnitude of the correction factor accounting for the proton energy loss and X-ray absorption in the bulk of the hair is formulated; 2) A simple method to qualitatively determine the transverse distribution of each trace element in a hair is introduced and proved to be very successful; 3) Proton back-scattering is proved to be capable of providing an ideal linear measure of the geometric hair diameter, one of the most important parameters in quantifying the results of PIXE measurements in mass concentrations. This technique satisfies the demands raised in the introduction: it can not only determine the small amount of a trace element in a hair, but also to a certain extent assay the endogenous or exogenous origin of the element.

Paper I

In this paper the accuracy of the PIXE method applied to a single hair strand is discussed in detail. The discussion is supported both by demonstrating the details in calculating F , the correction factor, in cases where the trace element is uniformly distributed in the bulk of the hair, and by showing the results of PIXE analysis of single hair strands for sulphur and zinc. The geometric diameter of a hair strand is shown to be a more suitable parameter than the linear density in the quantification procedure. It is concluded that the accuracy of the PIXE method does not become considerably lower when it is applied to a single hair strand. Thus accuracy and precision below 10% can be achieved.

Paper II

In this paper it is shown both theoretically and experimentally that the distribution of a trace element over the transverse cross section of a hair can be qualitatively determined by performing PIXE measurements at two different proton energies. A parameter is introduced to qualitatively describe the distribution of a trace element over the transverse cross section of a hair. The parameter is also used in an evaluation of the correction factor by linear interpolation.

Paper III

In this paper it is shown both theoretically and experimentally that the intensity of the back-scattered protons from a surface layer of a hair, which corresponds to the number of counts between two chosen channels in the observed proton back-scattering spectrum, is linearly proportional to the diameter of the hair, and thus provides a convenient tool for determining the most important parameter in quantification of the results of PIXE analysis of single hair strands.

Paper IV

In this paper the PIXE system designed and constructed for routine longitudinal scanning of single hair strands is described. It is a realization of the concepts developed in the above three papers. The technical measures to reduce the heating damage, to obtain a homogeneous beam profile while maintaining the necessary beam intensity, and to correctly integrate the electric charge etc. are also described.

References

S.A.E. Johansson, Ed. Proc. of "the First International Conference on Particle Induced X-Ray Emission and Its Analytical Applications", Nucl.Instr. and Meth. 142 (1977) 1.

S.A.E. Johansson, Ed. Proc. of "the Second International Conference on Particle Induced X-Ray Emission and Its Analytical Applications", Nucl.Instr. and Meth. 181 (1981) 1.

B. Martin, Ed. Proc. of "the Third International Conference on Particle Induced X-Ray Emission and Its Analytical Applications", Nucl.Instr. and Meth., to be published (1983).

J.W. Copius Peereboom, Ed. "Trace Element, Health and Hair Analysis", Proc. Int. Symp. (Amsterdam, 1982).

A.C. Brown and R.G. Crounse, Eds. "Hair, Trace Elements and Human Illness", Proc. of the Second Human Hair Symposium, (Preager, New York, 1980)

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A QUANTITATIVE BASIS FOR HAIR ANALYSIS USING PIXE

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The PIXE technique offers the possibility of scanning a single hair strand longitudinally with a millimetre proton beam for trace elements. However, the accuracy of the method has been questioned since the quantification of the mass concentration has been a serious problem. In this paper a specific beam-hair-detector geometry is assumed, and the correction factor accounting for the proton energy loss and the X-ray absorption in the hair is calculated. 43 hair segments from 8 individuals, ranging from 45 to 110 μm in diameter were analyzed giving a mean value of 4.32% (standard deviation 0.25%) for sulphur, and a mean value of 149 ppm (standard deviation 35 ppm) for zinc. It is shown that the geometrical diameter of a hair strand is a more suitable parameter than the linear density in the quantification procedure, and that the corrections for the effects of proton energy loss and X-ray absorption in hair are important not only for the determination of the absolute elemental concentrations but also for the determination of their relative longitudinal distributions. The uncertainty in converting the characteristic X-ray intensities to absolute elemental concentrations due to the complexities of the properties of human hair is evaluated. Possible ways of reducing this uncertainty are also discussed. It is concluded that the accuracy of the PIXE method does not become considerably lower when it is applied to single hair strands. Accuracy and precision below 10% may be reached by implementing the procedure and technical measures described.

*On leave from Department of Nuclear Physics, Fudan University, Shanghai, China.