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ANALYSIS OF TRACE ELEMENTS IN HUMAN HAIR BY PIXE*†

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ABSTRACT. The PIXE method was applied to the analysis of trace elements in scalp hair using two methods for target preparation. In the first method eigth hair strands each with nearly cylindrical geommetry and approximately the same diameter were selected and placed on an aluminum frame. In the second method a given mass of hair was dissolved with nitric acid and a known amount of strontium was added to the solution and dripped on a membrane filter using a micropipet. The results for the concentrations of trace elements in hair obtained by the two methods are compared and several aspects of the analysis is discussed.

RESUMO. O método PIXE foi aplicado à análise de elementos traços em cabelo utilizando-se duas técnicas diferentes para a preparação do alvo. A primeira técnica consiste na escolha de oito fios de cabelo, cada um com geometria cilíndrica e aproximadamente o mesmo diâmetro, que são colocados numa estrutura de alumínio. A segunda técnica consiste na dissolução de uma dada massa de cabelo em óxido nítrico, na marcação da solução resultante com uma quantidade conhecida de estrôncio e deposição posterior sobre filtro de membrana utilizando-se uma micropipeta. Os resultados obtidos para as concentrações de elementos traços através do uso das duas técnicas são comparados e os diversos aspectos da análise são discutidos.

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INTRODUCTION

The analysis of scalp hair by PIXE has been suggested as an alternative method for research and monitoring contamination of trace elements in man[1]). When this method is used for a large number of samples, the conditions for a reliable analysis need to be found. Two different methods for target preparation for analysis of hair samples by PIXE are described. In the first method, eigth hair strands with nearly cylindrical geommetry each were placed on an aluminum frame with regular spacing. In the second method a given mass of hair was dissolved with nitric acid and a known quantity of strontium nitrate was added to the solution[2]); the solution was then dripped on a Nuclepore membrane filter using a digital micropipet. Both targets were irradiated with a 2 MeV proton beam produced by a Van de Graaff accelerator.

The total hair mass irradiated was obtained, in the first case, from the knowledge of the length of the hair irradiated the measure diameter and the average hair density. The corrections for X-ray self absorption and loss of energy of the incident proton beam with penetration depth was also introduced using a previously described approach[3]).

The hair irradiated was obtained, in the second case, from the known mass of strontium added to the solution.

The results of the analysis for the determination of hair contents using the two different target preparation methods, are compared for several samples. The results of the analyses for a large number of samples, using the second method for target preparation, are also presented. These results are then compared with: the results of the analysis, by the same method, of a reference hair sample furnished by the IAEA; and the Reference Man data for hair elemental composition.

EXPERIMENTAL PROCEDURE

The hair samples used in the present analyses were selected from a large number of samples collected in a region of Mexico. Each hair sample was washed in accordance to the procedure suggested by the IAEA[1]) , then dried at room temperature and stored in a closed container.

In the first method, the target was prepared by selecting eigth hair strands from one subject with nearly the same diameter with the aid of a microscope and placed, with regular spacing, on an aluminum frame to fit the irradiation chamber. Since hair is a poor electrical conductor, it was observed positive charge accumulation from absorbed protons during irradiation. The resulting discharges produce a white background radiation which interfer with the characteristic X-ray spectra. This charge build up was avoided by an spray of electrons produced by a thin aluminum film placed on the collimator near the target.

In the second method, approximately 60 mg of hair was dissolved in 1 ml of pure nitric acid to which 20µl of a solution containing strontium was added. The strontium solution was prepared, adding 150 mg of strontium nitrate,$Sr(NO_3)_2$,in 1 ml of bidistilled water. The target itself was prepared by dripping 5.0µl of the final solution on a Nuclepore filter 0.4µm pore size mounted on an Aluminum frame 1.2 cm diameter. The purity of the nitric acid and the strontium solution was checked by establishing background spectra of two targets prepared with 5µl each,one with nitric acid and the other with the strontium solution, which were dripped on Nuclepore filters and irradiated under the same conditions of the overall experiment.

All targets were irradiated with a 2 MeV proton beam supplied by 4.0 MV Van de Graaff accelerator. The characteristic X-ray spectra was measured with a Si(Li) detector with 175 eV resolution at the 6.4 keV line of Fe, placed at a 90° angle with the direction of the proton beam. The overall experimental arrangement is the same as described elsewhere4) .

In the irradiation of the targets prepared with hair strands placed on an aluminum frame was used a tantalum collimator with a square hole 2 mm side, which permits to know the irradiated hair length. A tantalum collimator of 4 mm diameter was used in the irradiation of the targets prepared according to the second method.

RESULTS AND DISCUSSION

A group of samples randomly selected was analysed using both methods described in the preceding section and the values obtained for the concentrations of the detected elements are shown in Tables I and II.

The basic expression for determining elemental concentrations in hair by PIXE is the same generally used5) and, for convenience, is rewritten here for the elemental mass M given in μg as follows.

$$M = 2{,}66 \times 10^{-9} \frac{A\ S\ N_x}{\frac{\Omega}{4\pi}\ \varepsilon\sigma_x(E)\ Q\ F}$$

where:

A is the atomic mass of the element; S is the collimator are in mm^2; N_x is the number of characteristic X-rays detected; Ω is the solid angle defined by the detection system; ε is the detection efficiency excluding the geommetrical factor $\Omega/4\pi$; $\sigma_x(E)$ is the X-ray production cross section for incident particles with energy E given in barns; Q is the integrated mean charge in μC; and F is the correction factor due to effects of X-ray self absorption and particle energy loss with penetration depth3,6).

When hair strands are used as targets,it is necessary to know the hair density to obtain the elemental concentration, since the diameter is measured and the hair strand length irradiated is defined by the collimator. In the results presented in Table I the density was taken as that of the Reference Man^{7}). However, the hair density varies significantly from sample to sample and, as a consequence, introduces errors in the results presented in Table I. In addition to that, since hair strands can be considered a thick target for irradiation with a 2 MeV proton beam, the effects of proton energy loss with penetration depth and characteristic X-ray self absorption have to be considered. These effects were taken into account in accordance with the procedure suggested by Montenegro et al^{3}). The mass attenuation coefficients for characteristic X-rays were obtained from tabulated values^{8}) and averaged assuming the following basic composition of hair: Carbon (49.0%), Nitrogen (14.5%) and Oxigen (30.0%)^{7}). The values of the X-ray production cross sections are taken from reference^{9}).

In this method for target preparation, the amount of elements in the hair target irradiated is only in the nanogram range, therefore requiring long irradiation periods. The results shown in Table I required irradiation periods of the order of six hours per target. These long irradiation periods are necessary because hair is a poor thermal conductor and may burn if a high beam current is used. The beam current in this experiment was of the order of 30 nA.

In the second method of target preparation most of the difficulties described above are eliminated. A thin target can be obtained with a larger mass of hair (≈ 300μg), therefor reducing the effects of proton energy loss and X-ray self absorption, which allows to neglect the corrections due to thes effects. The time of irradiation was reduced to about one orde of magnitude to obtain a spectra with counting statistics comparable that obtained with the other method described. Furthermore, the preparation of the target is simplified avoiding the time consuming selection of hair strands with same diameter required in the first method. Another advantage is the fact that the mass of each element is determined from the known mass of strontium added to the hair solution and req only the relative detection efficiency which can be determined with higher precision than the absolute efficiency.

The main source of the discrepancy between the values shown in Tables I and II can be atributed to the use in the first method of the averaged value of the hair density. The averaged value for the elemental concentrations, presented in the last line of Tables I and II show consistenly lower values for the results obtained with the first method of target preparation.

Possible contaminations of the strontium solution where checke by preparing five targets with the strontium solution and irradiating under the same conditions of the overall experiment No contamination was detected in all five analysis which assur the purity of the strontium solution. In addition to that, one may conclude that the Nuclepore filters used did not present detectable contamination either. Similar procedure was adopted to the nitric acid used.

The method of dissolving the hair sample in nitric acid and add a known amount of strontium to the solution, has proved to be more convenient to analyse a larger number of samples. This procedure was adopted in the analysis of forty samples. The results obtained are summarized in table III, where only the maximum, the minimum and the average values for the concentration of the elements detected are shown. In last two columns of table III are presented the elemental concentrations resulting from the analysis of the IAEA HH1 reference hair sample and data taken from the Reference Man7). Those values are within the range of values obtained in the analyses of the hair samples from Mexico. However, the averaged values for the latter are generally higher than those for the Reference Man, and very close to those of the IAEA reference sample.

The estimated error in the elemental concentrations measured are: in the first method of the order of 25%; and the second method 15%

CONCLUDING REMARKS

The analysis of trace elements in hair by the PIXE technique using the two described procedures for target preparation offers the basis to comment about important aspects that should be considered when applying this technique.

The two procedures for target preparation give results for the trace element concentrations that are within the same order of magnitude. However, the second method, where the hair sample is dissolved in nitric acid, has proved to be more convenient for routine analysis. Furthermore the time required for irradiation is shorter and the error in the measurements can be minimized since, the elemental concentratio is obtained from the total mass of hair and the total amount of strontium used in the solution. In the first method for target preparation, when hair strands are used, the density, diameter and length of the irradiated hair have to be known to determine the trace element concentrations. These parameters are difficult to measure and therefore introduce significant errors. In addition to that the corrections due to the effects of energy loss with penetration depth and X-ray self absorption are generally large. These corrections are also difficult to estimate since the actual trace element distributions within hair are generally unknown, and as a consequence the corrections can only be determined with certain range of uncertainty. In the present work these corrections were taken into account assuming homogeneous distribution of trace elements and a perfect cylindrical hair. The correction can be as high as one hundred percent.

As a closing remark we want to emphasize that when the PIXE method is used for the analysis of trace elements in hair, careful attention has to be maintained in the target preparation procedures. When using each the of the two methods described in the present article one is able to detect most of the trace elements, however, it was also verified that in some cases the results obtained differ significantly for each single method. The method of dissolving hair in nitric acid gives the averaged distribution of trace elements in a considerably large mass of hair; whereas the analysis by the other method is limited to a reduced number of hair strands as well to a reduced length of the hair strands selected. Since the elemental concentration may vary from hair to hair in the same subject as well as along the hair length of one strand some discrepancies which appear in the corresponding results of Tables I and II may be explained by the fact that Table I reflects local elemental hair concentrations while Table II refers to average values. Therefore, care must be exercised in the appropriate choice of target preparation, depending on the ultimate information desired.

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Table I. Elemental concentration of trace elements in hair, in mg/g, obtained using targets prepared by placing eight strands on an aluminum frame (first method).

	Hair elemental concentration (mg/g)						
Identification	Ca	Cr	Mn	Fe	Ni	Cu	Zn
Z-V-2-F	3.4	0.029	n.d.	0.088	n.d.	0.024	0.24
Z-V-7-A	0.35	0.0090	n.d.	0.013	n.d.	0.018	0.14
Z-V-7-J	0.35	n.d.*	n.d.	0.039	n.d.	0.070	0.19
Z-V-6-A	0.65	n.d.	n.d.	0.027	n.d.	0.023	0.36
Z-V-2-H	0.50	n.d.	n.d.	0.020	0.011	0.017	0.24
F-I	2.0	n.d.	0.0061	0.048	0.0025	0.026	0.17
Z-V-5-H	1.9	n.d.	0.0060	0.095	0.0019	0.037	0.35
F-E	2.7	n.d.	n.d.	0.056	0.0019	0.060	0.51
Average	1.5	0.019	0.0060	0.048	0.0043	0.034	0.27

* n.d. = not detected

Table II. Elemental Concentration of trace elements in hair, in mg/g, obtained using targets prepared with a solution of hair in nitric acid to which a known amount of strontium was added (second method).

	Hair elemental concentration (mg/g)						
Identification	Ca	Cr	Mn	Fe	Ni	Cu	Zn
Z-V-2-F	1.1	n.d.*	n.d.	0.054	0.0077	0.015	0.24
Z-V-7-A	3.4	n.d.	n.d.	0.18	0.0095	0.099	0.58
Z-V-7-J	0.46	n.d.	0.0093	0.054	0.0037	0.055	0.16
Z-V-6-A	0.81	n.d.	n.d.	0.095	0.0037	0.018	0.17
Z-V-2-H	0.93	n.d.	0.0093	0.054	0.0037	0.022	0.23
F-I	2.6	n.d.	0.0074	0.029	0.0037	0.035	0.23
Z-V-5-H	1.4	n.d.	n.d.	0.11	0.013	0.044	0.40
F-E	2.2	n.d.	n.d.	0.075	0.013	0.051	0.47
Average	1.6	-	0.0087	0.081	0.0073	0.042	0.31

*n.d. = not detected

Table III. Maximum, minimum and average elemental concentratio in mg/g, hair samples of forty subjects using the second method for target preparation. Also included are the hair elemental concentration of the IAEA reference sample analysed using the same method, and data from the Reference Man.

	Hair elemental concentration (mg/g)				
Element	Maximum	Minimum	Average	IAEA Reference Sample	Reference Man
Ca	12.3	0.27	2.1 (04)*	1.4†	3.2
Ti	0.019	0.019	0.019 (01)	n.d.	0.00050
Cr	0.22	0.012	0.062 (11)	0.019	0.0038
Mn	0.10	0.0033	0.027 (21)	n.d.	0.0013
Fe	2.0	0.033	0.20 (40)	0.098	0.030
Ni	0.044	0.0019	0.010 (28)	0.013	0.0075
Cu	0.099	0.0087	0.039 (38)	0.028	0.016
Zn	2.5	0.11	0.48 (40)	0.29	0.26
Br	0.071	0.071	0.071 (01)	n.d.	0.013
Pb	0.053	0.023	0.038 (02)	n.d.	0.050

* parenthesis indicates number of samples in which the element was detect

n.d. - not detected.

† average of six measurements as performed by this laboratory.