

Trace Elements in the Environment and Biomonitoring

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Objectives

An area where the PIXE technique presents an added value relative to others is biomonitoring or monitoring of elements in living organisms. It is therefore important to preserve the historical know-how in this field, but also to deepen the installed capacity, also because this area may configure itself as important for wider scopes in environmental problems. Activities under this title present strong collaboration with other groups both from within ITN as well as outside.

Results

In 2004, preliminary works were carried out to inspect the capacity of applying PIXE to open ocean plankton biomonitoring and to commercial vegetables and fish minor and trace element content monitoring. The test for PIXE applicability to plankton monitoring was carried out in collaboration with IPIMAR. Surface water samples were collected in geographical coordinates showing different water column heights. Sampling was carried out during a research ship campaign.

The sampling spots were selected in order to have a crude coverage of the whole Portuguese coast. Water samples were filtered using aerosol sampling equipment specifically adapted for the purpose. The results obtained for Fe are presented in Fig.1. These are similar to results present in the literature for similar conditions.

Published, accepted or in press work

1. A.P. Marques, M.C. Freitas, M.A. Reis, H.TH. Wolterbeek, T.Verburg, MCTTFA applied to differential biomonitoring in Sado estuary region, *J. Rad. Nucl. Chem.* **259** (2004) 35-40.
2. M.A. Reis, L.C. Alves, M.C. Freitas, B. Van Os, J. De Goeij, H.TH. Wolterbeek, Lichen *Parmelia sulcata* surface-layer model coefficients, in Proceedings of the III International Workshop on Biomonitoring of atmospheric pollution (with emphasis on trace elements) – IJS, LjubLjana 2004 (ed. in CD-ROM).

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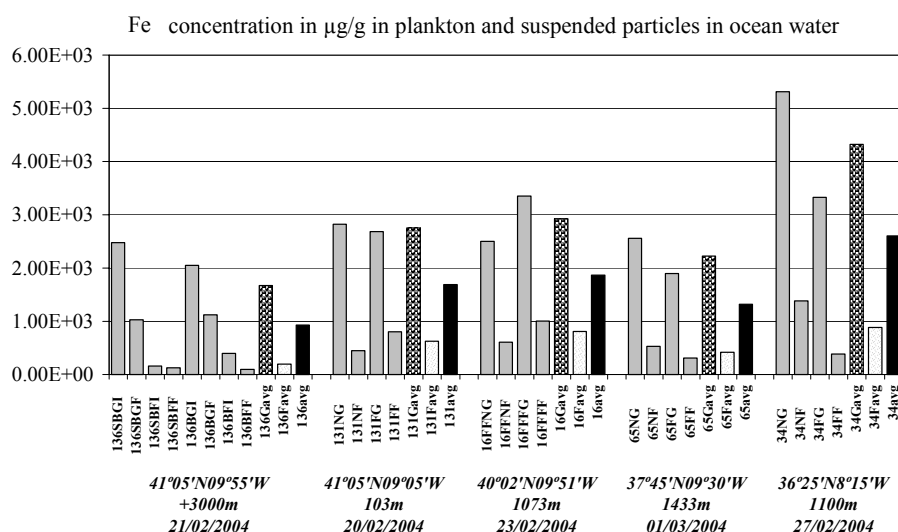


Fig. 1. Fe concentration in particulate matter filtered from water samples collected along the Portuguese shore in surface water at different water column heights. Sampling spot coordinates, water column height and day of sampling are presented for the five sampling locations used in the experiment. It can be seen that coarser particles (G reference) contain always a higher iron concentration than do smaller ones (F reference)

Laboratory for the Characterization and Speciation of Aerosols (LCEA) Part I - Speciation and HRPIXE

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Objectives

One of the major and more far reaching developments within PIXE is the quest for its application to speciation. This is also the aim of this sub-chapter of the workprogram of the LCEA. This workprogram is in execution since 2003, in spite the fact that the main project was only approved for funding during 2004. So far funding was limited to services, mecenass funding, and other small budget sources.

Results

One of the most interesting results in 2004 was obtained in the frame of an international collaboration with the Josef Stefan Institute in Slovenia. This cooperation made it possible to carry out an experiment in a ultra-high resolution wave length dispersive spectrometer where the variability of L x-rays line ratio was studied as function of the ion beam energy.

Results previously found for proton impact on W, using the Si(Li) detector and the PIXE set-up at ITN, could be corroborated in this way, for proton impact on Mo. The changing in $L\beta_{2,15}$, $L\beta_3$ and $L\beta_4$ spectra of Mo as function of beam energy are shown in Fig.1.

Published, accepted or in press work

1. M.A. Reis, P.C. Chaves, J.C. Soares, Particle Induced X-ray Emission – Relative Yield Ion Energy Dependence, an IBA chemical speciation method, *Nucl. Inst. and Meth. in Phys. Res. B* (in press)
2. P.C. Chaves, M.A. Reis, Comparative study of W-K and L shells relative yield ion energy dependence, in Proceedings of the X International Conference on PIXE and its Analytical Applications, Portorož, Slovenia, June 4-8, – IJS, Ljubljana 2004 (ed. in CD-ROM).

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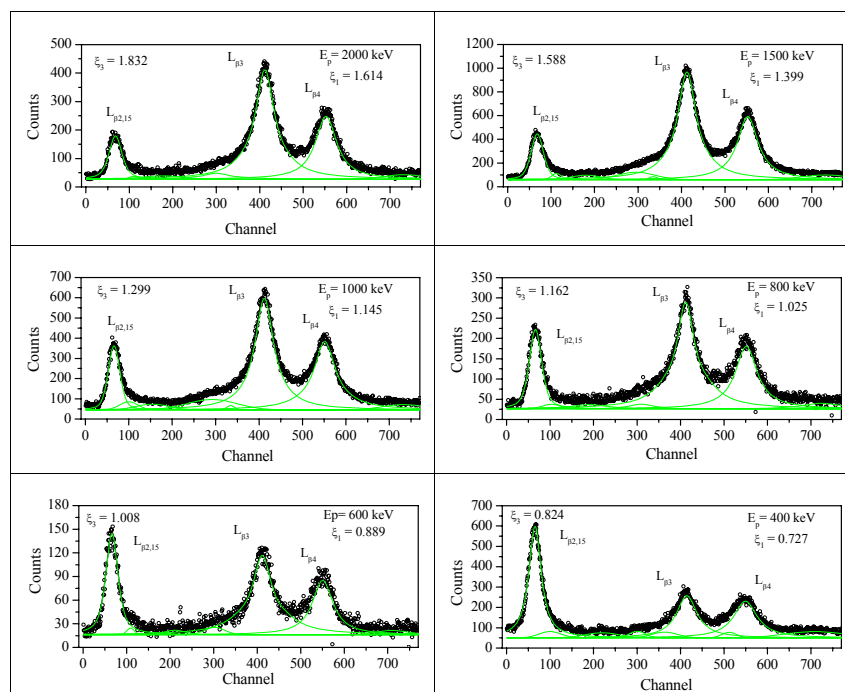


Fig. 1. $L\beta_{2,15}$, $L\beta_3$ and $L\beta_4$ spectra of Mo as function of proton beam energy. It can be seen that although $L\beta_3$ and $L\beta_4$ are transitions to the same L sub-shell, their ratio is not constant. The changes in $L\beta_{2,15}$ relative to $L\beta_3$ are also not reproduced by the calculations based on a previously published semi-empirical correction to L shell x-ray production cross section.

Laboratory for the Characterization and Speciation of Aerosols (LCEA) Part II – Aerosol composition monitoring

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Objectives

The second major item in LCEA is the implementation of a Low Cost Aerosol Sampling Network. In order to achieve this, a low cost aerosol sampler was developed in 2003 and is now under operation at ITN campus. The aim of this line of work is therefore the maintenance of the installed capacity for aerosol elemental composition monitoring, together with the research, development and demonstration of new approaches to monitoring and/or data handling. Simultaneously, the robustness of the ITN sampler is also tested under true working conditions. Activities under this title present a strong cooperation to other groups within ITN, namely the group using k0-INAA at the RPI.

Results

A significative parcel of the CEEFI work during 2004 was related to the PIXE analysis of airborne particulate matter (APM) within this scope. The monitoring protocol used was nevertheless slightly modified relative to what was being carried out in the previous years once no contract/legislation limitations are presently imposed. Sampling was carried out during 2004 in an intermitent (6 minutes on 18 minutes off) all days sampling. Filters are replaced every week.

In this way an almost continuous monitoring is achieved. In parallel to this, a database structure, which includes samples historic record, was created. Presently it only remains to be carried out a thorough revision of all the structure (data and data linkages) in order to have the database in conditions of being made available to general access. In Fig.1 the time series of week averages of Cl in airborne particles determined during 2004 is presented (as an example of part of the information that will be made available in a near future). This time series is nevertheless important in itself as it shows that from middle year forward repetitive events of very high Cl concentrations in fine particles were identified. This result may point towards a problematic situation or not, because no information is yet available on the chemical species carrying media of this chlorine. It nevertheless requires further investigation to trace its origin. Simultaneously, this result clearly shows the need for such a type of multi-element continuous monitoring of airborne particles composition.

Published, accepted or in press work

1. M.C. Freitas, S.M. Almeida, M.A. Reis, M.G. Ventura, Neutron activation analysis: Still a reference method for air particulate matter measurements, *J. Rad. Nucl. Chem.* **262** (2004) 235-239.

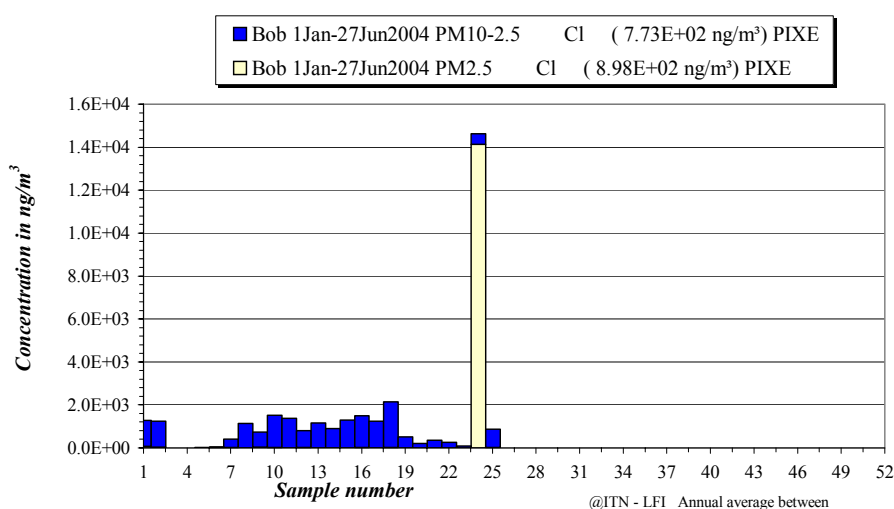


Fig. 1. Airborne chlorine week average concentration in PM10 specifying the PM2.5 component, determined at ITN during 2004

Laboratory for the Characterization and Speciation of Aerosols (LCEA) Part III – Technical support and thin films analysis

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Objectives

A third objective of the LCEA project refers the use of the PIXE set-up and its developments for uses other than aerosol studies. One of the more immediate and important application of the whole developments carried out to improve the capabilities of analysing aerosols is the analysis of very thin films, which cannot be fully characterised by other IBA techniques. Specific developments are also considered for this purpose.

Results

Within 2004 and in this context, more than 14 different works were carried out at request of other groups, 8 of these being thin film analysis. This fact promoted the development of a specific sample holder for the measurement of thin films in grazing detection conditions, made in 2004.

Fig.1 presents results for one of the most complex types of targets analysed, namely a GaAs-InSb films existing on top of a GaSb substrate. In this case PIXE is not able to provide a single answer but still it is possible to define the As and In concentration as function of the film tickness.

Published, accepted or in press work

1. M.A. Reis, P.C. Chaves, V. Corregidor, N.P. Barradas, E. Alves, F. Dimroth AND A.W. Bett, Detection angle resolved PIXE and the equivalent depth concept for thin films characterization, *X-ray Spectrometry* (in press)
2. M.A. Reis, P.C. Chaves, V. Corregidor, N.P. Barradas, E. Alves, F. Dimroth AND A.W. BETT, Grazing detection geometry for PIXE characterization of thin films, in Proceedings of the X International Conference on PIXE and its Analytical Applications, Portorož, Slovenia, June 4-8, – IJS, LjubLjana 2004 (ed. in CD-ROM).
3. P.C. Chaves, O.R. Oliveira, V. Corregidor, N.P. Barradas, M.A. Reis, CdTe detector use in PIXE characterization of Sn doped CdO thin films, in Proceedings of the X International Conference on PIXE and its Analytical Applications, Portorož, Slovenia, June 4-8, – IJS, LjubLjana 2004 (ed. in CD-ROM).

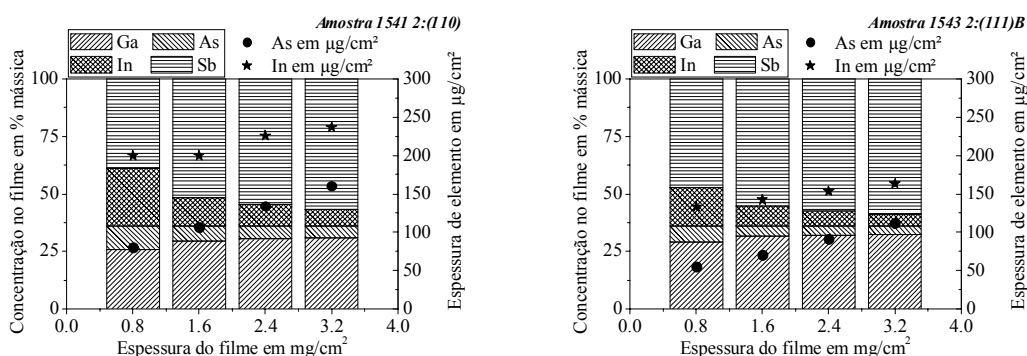


Fig. 1. As and In concentration as function of the film tickness in GaAs-InSb films existing on top of a GaSb substrate.