Elemental Characterization and Speciation Using Ion Beams - CEEFI

Miguel A. Reis

The Elemental Characterization and Speciation Using Ion Beams group (CEEFI) was born in the sequence of a small reorganization of activities using the 2.5 MV Van de Graaff accelerator of ITN, namely in what concerns activities previously in the framework of the Atmospheric Elemental Dispersion (DEA) unit.

CEEFI carries out work of research, development and application of ion beam based nuclear analytical techniques for the characterization of samples elemental composition, aiming also at speciation methodologies. Main focus is put on particle induced x-ray emission (PIXE) and in atmospheric environment related samples (airborne particulate matter and atmospheric biomonitor samples).

In complementary lines of work, the group assumes that it is important not to depend exclusively on collaborations neither for sampling nor for data handling processes. Therefore, R&D is carried out on airborne particles sampling and on data handling methods, both for spectra handling and for aerosol and biomonitor multielementar data analysis.

Taking into account that PIXE is already a matured analytical technique, services are provided to both the community in general, and the scientific community in particular. In this last case, the analysis of samples other than environmental is carried out, and case studies do sometimes lead to spin offs associated to details or specific developments of the PIXE technique.

Within the organics of the Ion Beam Laboratory (LFI), CEEFI is responsible for the maintenance and improvement of the PIXE line, assuring that (at least) there are no losses on the installed capacity.

In 2003, the groups' activities have been structured on three main blocs: (a) PIXE analysis of airborne particulate matter (partially under contract) and optimization and quality control improvement of ITN PIXE set-up; (b) development and application of data analysis methodologies, including the inference of airborne elemental concentration statistics out of biomonitoring data; (c) launching the work program of the Laboratory for Characterization and Speciation of Aerosols within the limits of a ultra-tight budget (limited to the auto-financing share, as the specific funding proposal was not yet evaluated, inspite the fact that it was submitted in the first semester of 2002).

Within item (c), three major developments were carried out, namely: the establishing of a new methodology for elemental chemical speciation using ion beams, the construction and test of a second (improved) prototipe of the ITN aerosol sampler and the starting steps for the design and implementation of a HRPIXE system (High Resolution PIXE).

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Research Team

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Research Projects:	0
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	(17827.91) (invoices emitted but not paid up to 10.Dez)
Total:	**34757.22**

Publications

Books:	1
Journals:	7 and 1 in press
Proceedings:	4
Conf. Communications:	1
Other publications:	1
Theses:	Graduation 1

Airborne particulate matter analysis, optimization and quality control of the ITN PIXE set-up

M. A. Reis, P. C. Chaves, O. R Oliveira, R. Pinheiro
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Objectives

A significative parcel of the CEEFI work during 2003 was related to PIXE analysis of airborne particulate matter (APM) under contract. In parallel to this, progressively tighter quality control operations were implemented and it was identified that ITN PIXE set-up required some changes in order to improve quality assurance. In order to assure good quality of the large database being generated due to the 5 years measurements of APM samples, a database structure, which includes samples historic record was recognised as fundamental, and therefore aimed at. Activities under this title present a strong cooperation to other groups within ITN, namely the group using k_0-INAA at the RPI.

Results

During 2003, results obtained during 2002 and reported in Almeida et al. (2003) were carefully analysed and further supported with additional comparison between PIXE and k_0-INAA data. As a result of these apporach, the beam spot quality was identified as a strong candidate to source of fluctuations in APM data quality. A new back window, which includes a quartz viewer, was thus implemented (Fig.1) to overcome this problem

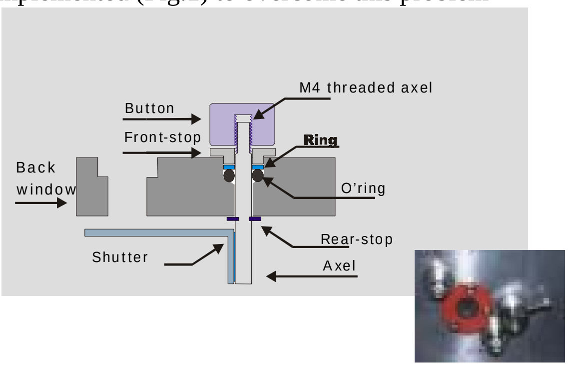

Fig.1: Shutter command button schematics; Back-window's rear view: quartz aperture and insulator (red), and BNCs for electric connections.

Once this was achieved, it was recognised that small tunning of the chamber alingment was required with a higher frequency than should be expected from the rate of accelerator maintenance. Improvements in the chamber positioning and alingment system were therefore projected and implemented. This includes the introduction of a stress free front holder and a completely new back holder (Fig.2).

Fig.1: View of the back holder and chamber

In respect to the historical records quality control, a year base structure was implemented. Due to the large number of values pertaining to each sample, a frequent redundance steps approach was used for quality assurance. Whenever possible, data comparison is carried out automatically and a 0 is obtained when two redundant records are equal. This allows the identification of random errors that could hardly be detected otherwise. The level of human data manipulation was reduced to the minimum and to one level only, which is the raw data level.

Data quality cheking is then supported by an exaustive historical record, which contains all information relative to each and every sample, therefore allowing a thorough inspection of all possible erroneous data, or otherwise confirmation of the significance of outliers.

The database structure was finished in 2003 and its use to generate the full 5 years database on airborne elemental concentration of trace elements, was started. Data is based on samples collected under contract (for the Non-continuous Air Quality Monitoring Program of S. João da Talha Urban Residues Incinerator), but results will be available for much more elements than those reported under contract.

Published, accepted or in press work

1. S.M. Almeida, M.A. Reis, M.C. Freitas, C.A. Pio, Quality assurance in elemental analysis of airborne particles, *Nucl. Inst. and Meth. in Phys. Res.*, **B 207** (2003), 434-446
2. S.M. Almeida, M.C. Freitas, M.A. Reis, C.A. Pio, Quality assessment on airborne particulate matter of k0-INAA, *J. of Rad. Nuc. Chem.*, **257** (2003) 609-613

[1] ITN-RPI Sector

Atmospheric biomonitoring and biomonitors response

M. A. Reis, O. R Oliveira, R. Pinheiro
C. Costa[1], A.P.Marques[1], I. Díonísio[1], M. C. Freitas[1]

Objectives

Access to information on air quality over wide areas is a complex subject. Dispersion modelling is the usual tool. In what refers to in field measurement, biomonitoring is one of the few if not the single tool available to approach the question. Within this title, CEEFI work aim at being able of discribing some airborne related parameters (e.g. atmospheric elemental concentration statistics) out of biomonitor data. Activities under this title present a strong cooperation to other groups within ITN, namely the group using k_0-INAA at the RPI.

Results

Most of the group's publications within 2003 were a result of this collaboration due mainly to the fact that in 2002 both groups were organically bound within ITN and this was, up until recently, the main line of work of the groups' head.

Apart from the already published results, during 2003 it was possible to apply a biomonitors calibration obtained previously, in order to infer the statistics of airborne elemental concentrations from data on lichen transplants exposed in the region of the Sado Estuary during 9 months. Data for S is presented in Fig. 1, it can be seen that the location of the (expected) major source for this element, the fuel based thermal power plant, is well identified in the standard deviation mapping, while the major average impact is identified as occuring further away from the source. Considering that the power plant has a 200m of hight stack, these results are fully compatible to what should be expectable.

The publication of these results was started but due to the multidisciplinary nature of the approach used to achieve these results, it was not yet possible to have the manuscript accepted for publication and it is still under revision

Published, accepted or in press work

1. H.TH. Wolterbeek, J. Garty, M.A. Reis, M. C. Freitas, Biomonitors in Use: Lichens and Metal Air Pollution, in Bioindicators and Biomonitors, B.A. Markert and A.M. Breure, H.G. Zechmeiter (Eds.), Elsevier Science B.V. (2003), ch 11.
2. M.A. Reis, L.C. Alves, M.C. Freitas, B. Van Os, J. de Goeij, H.TH. Wolterbeek, Calibartion of lichen transplants considering faint memory effects, Proceeding of the II Int. Workshop on Biomonitoring of Atmospheric Pollution (with emphasis on trace elements) – BioMAP II, IAEA-TECDOC-1338, (2003), pp. 105-117.
3. M.A. Reis, M.C. Freitas, J. DE Goeij, H.TH. Wolterbeek, Surface-layer model of lichen uptake, modelling Na response, Proceeding of the II Int. Workshop on Biomonitoring of Atmospheric Pollution (with emphasis on trace elements) – BioMAP II, IAEA-TECDOC-1338, (2003), pp. 152-159.

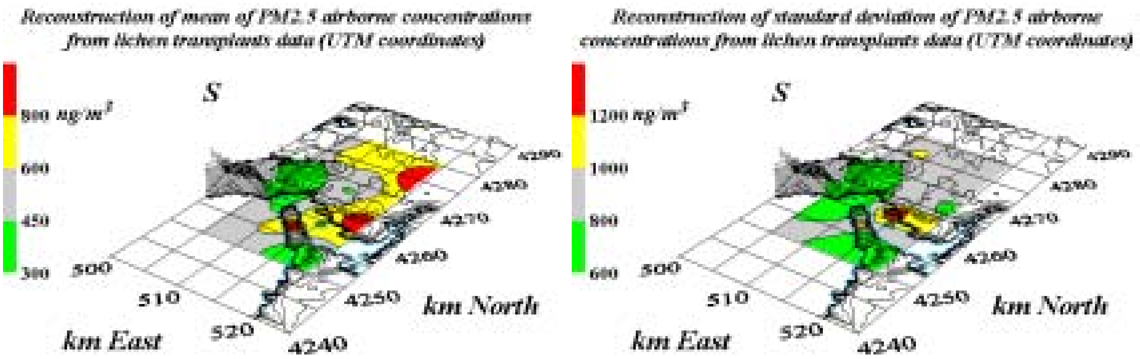

Fig.1 Mappings of the statististics for airborne S in PM2.5 infered from 9 months exposure of lichen transplants in the region of the Sado Estuary.

[1] ITN-RPI Sector

Laboratory for the Characterization and Speciation of Aerosols (LCEA) Part I - Speciation and High Resolution PIXE

P. C. Chaves, H. Pombo, M. A. Reis

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 (a project submitted to the 2002 reequipment program). This workprogram, in spite the fact that it was not yet evaluated for external funding, is nevertheless in execussion, as far as available funding allows.

Results

The main results achieved in 2003 within this framework were the establishment of a methodology for speciation of elements analysed through their L-shell spectra, and the first steps towards the implementation of a HRPIXE unit.

In what concerns the speciation methodology, the result was that ion beam energy scans provide patterns of variation of the line intensity ratio, which contain information on the chemical environment of the emitting element (Fig. 1). These results were obtained within a graduation work presented in July 2003.

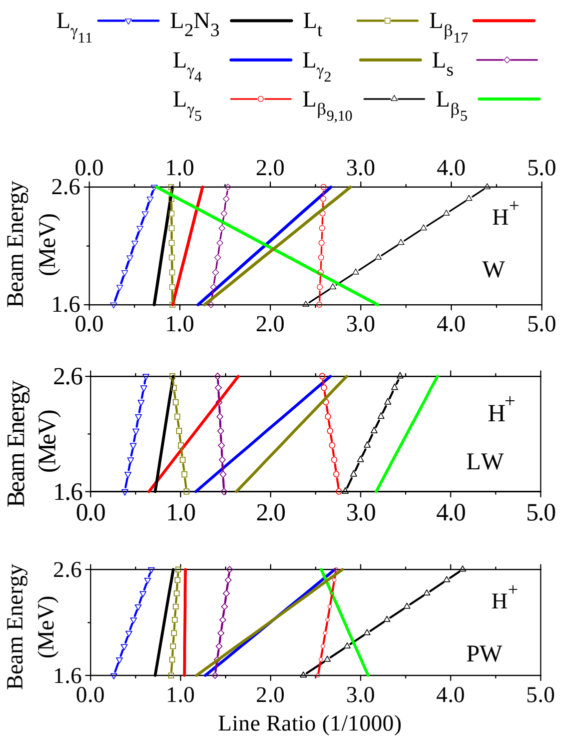

Fig. 1 Intensity Ratio Variation Patterns for: pure W, Li_2WO_4 (LW) and $P_2O_5 \cdot 24WO_3 \cdot xH_2O$ (PW)

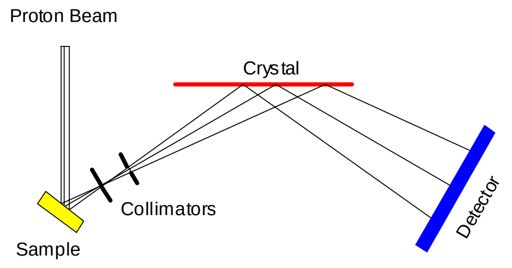

Fig.2: Scematics of a two colimators one crystal Bragg difratometer.

Relative to the HRPIXE design, a software code was implemented and run in order to start optimizing the options existing in what concerns the distance between the detector and the sample (x-ray source). This which was shown to be the single parameter controlling relative resolution, for a fixed Bragg diffraction angle and collimators, set.

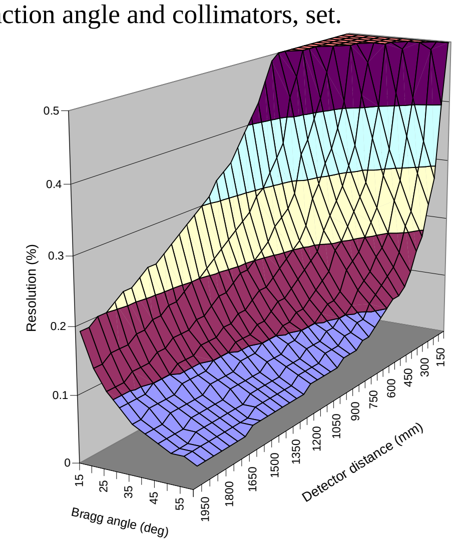

Fig.3: Relative resolution of the 2 collimators 1 crystal difratometer for a first colimator of 0.5 mm and the second wide open.

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1. P.C. Chaves, Especiação química com PIXE – métodos, requesitos e viabilidade, Graduation in Physics Engineering, Fac. of Sciences of the Univ. of Lisbon, July 2003. Supervisors: Dr. Miguel A. Reis (ITN) and Prof. José Carvalho Soares (FCUL).

2. M.A. Reis, O.R. Oliveira, P.C. Chaves, H. Pombo, CEEFI Annual Report 2003, ITN Report N. ITN/Física/001/2003

Laboratory for the Characterization and Speciation of Aerosols (LCEA) Part II – Low Cost Aerosol Sampler

O. R. Oliveira, M. A. Reis, P. Matos[1], M. L. Botelho[1]

Objectives

The second major important item in LCEA is the implementation of a Low Cost Aerosol Sampling Network. In order to achieve this, a low cost aerosol sampler is necessary. Due to the fact that these are not easily available in the market, but also because there is an extra cost (may reach a farctor of 2 or more) to acquire samplers in the market, an ITN sampler was developed. In this context, acquisition of know-how on aerosol sampling (in both outdoors and indoors) is also aimed at.

Results

During 2003, the previously developed prototipe was corrected for some identified deficiencies or cumbersome solutions and tested against Gent sampler based machines.

Fig.1: ITN-URSA sampler, is used with a INT-PM10 separator head capable of slight heating the influx or the front filter to prevent clogging due to water drops formation on the filter.

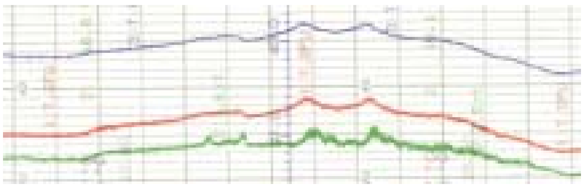

Fig.2: URSA/PM10-Impactor heating test for 10Vdc heater's voltage supply and 12LPM: red-coarse fraction filter temperature (T1), blue-heater temperature (T2), green–outside temperature.

This prototipe (URSA) revealed itself a quite versatile machine, being possible to use also for indoor test of clean/controled rooms, including the evaluation of the determination of the number of collony forming units.

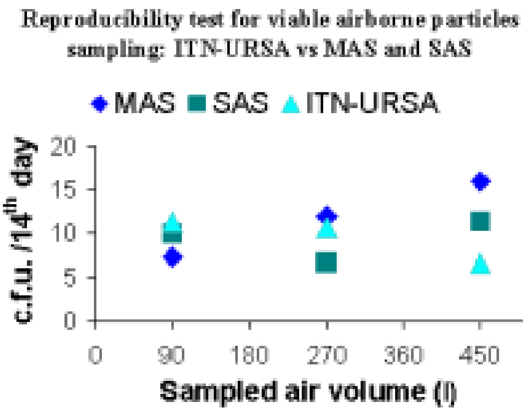

Fig.3: Comparison of results obtained by using URSA and the well known MAS (Merk Air Sampler) and SAS (Surface Air System) used for the determination of collony forming units (c.f.u.) in a controled room test.

Test comparing the performance of ITN-URSA system to the previously used Gent system started and are being carried out exaustively.

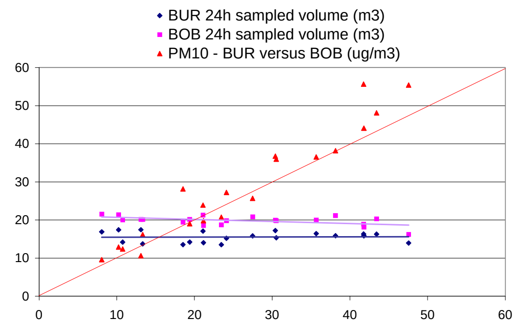

Fig.2: URSA/PM10-Impactor heating test for 10Vdc heater's voltage supply and 12LPM: red-coarse fraction filter temperature (T1), blue-heater temperature (T2), green–outside temperature

Published, accepted or in press work

1. M.A. Reis, O.R. Oliveira, P.C. Chaves, H. Pombo, CEEFI Annual Report 2003, ITN Report N. ITN/Física/001/2003
2. P. Matos, M.L. Botelho, 1st Report preliminary studies for environmental control in the Portuguese Army Hospital, October 2003

[1] ITN-Physics Sector

Laboratory for the Characterization and Speciation of Aerosols (LCEA) Part III – PIXE set-up upgrade and thin films analysis

P.C. Chaves, O.R. Oliveira, M. A. Reis, V. Corregidor, N. Barradas, E. Alves

Objectives

A third objective of the LCEA project is refered to the use of the PIXE set-up developments for other uses. One of the more immediate 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.

Results

Within 2003 a double detector window was designed and build and a new CdTe detector was calibrated and tested.

Fig.1: View of detectors window and sleeve.

The double detector design still considers the add of a magnetostatic particle deflector to be placed in front of the Si(Li) detector in order to allow the measurement of very low energy x-rays (Na).

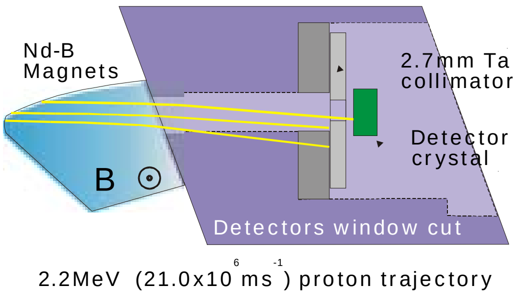

Fig.2: First scematics of the magnetostatic deflector.

The CdTe detector is particularly fit to the measurement of high energy x-rays, therefore aiming at using K x-ays for cases where usually L x-rays are used.

Table I: Comparison of results obtained with the CdTe and the Si(Li) detectors.

Sample	In ($\times 10^{15}$ at/cm^2)	As ($\times 10^{15}$ at/cm^2)
1182_gisab_1 (Si(Li))	128(6)	46(2)
1182_gisab_1(CdTe)	133(6)	45(3)

The first results obtained with the new CdTe detector were compared to the ones obtained with the previous Si(Li) detector. In the case study used for comparison, namelly In-As-Ga-Sb thin films (Fig.3) measurements in grazzing detection conditions, it can be seen that not much improvement was achieved in this first test. Still, because the electronic coupling of the CdTe detector is not as straightforward as the one for the Si(Li), there is much room for improvement.

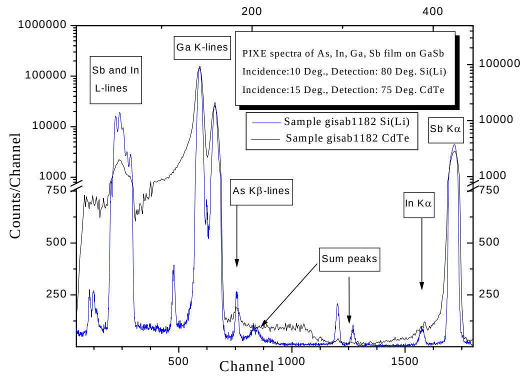

Fig3: PIXE spectra of As, In, Ga, Sb films on GaSb. Comparison of the Si(Li) and CdTe spectra.

Published, accepted or in press work

1. C. Liu, T. Matsutani, T. Asanuma, K. Murai, M. Kiuchi, E. Alves, M.A. Reis, Room-temperature growth of crystaline indium tin oxide films on glass using low-energy oxygen-ion-beam assisted deposition, J. of App. Phys., 93 (2003) 2262-2266