

Neutron Activation in Environment, Nutrition and Epidemiology

Maria do Carmo Freitas

The research is focused on development of methodologies in neutron activation analysis and their application to studies of atmospheric environment, nutrition and health. The investigation appeared as a natural application of the potentialities of k_0 -INAA (instrumental neutron activation analysis using the k_0 -method). The unit activities include six main lines:

Development of Methodologies, Quality Control, Automatization, Data Handling aim to optimize the technique in order to enable the measurement of numerous samples measured and to speed the calculation and handling of the data. Also it aims to extend to other methodologies in order to improve the detection limits for important chemical elements as cadmium, arsenic, nickel as well as to turn possible to determine lead and the light elements. Steps are being given towards ISO 17025 to establish protocols and standard procedures. Exercises of interlaboratory data comparison are targets.

Monitoring, Biomonitoring aims to characterise areas of Portugal using lichen transplants, air particulate matter collection, and (wet+dry) deposition. The data are analysed for factors aiming at identifying emission sources and the spread of elements through the atmosphere, both locally and by long-range transport. Data analysis methods and their development are very important due to the multielement nature of the analytical technique used. To assure the quality of the data, accuracy and precision studies are being performed, both in biomonitoring and monitoring fields, aiming at better understanding differences found in the results for the same element and sample. Air particulate matter obtained by different air samplers is compared. So-called conventional analytical techniques are applied to complement the research unit's results. New biomarkers are suggested and studied. Pb-210 is being determined to confirm terrestrial origin of aerosols. Within this activity line, the following is being done: services to industry/Universities, FCT funded project

research and Ph.D. theses in collaboration with Universities.

Epidemiological studies include health related problems. The objective is to link biomonitoring and monitoring to epidemiological studies, at local, regional and European scale. Currently, one PhD is dedicated to this subject and two projects on this subject are running, financed by FCT.

Element Uptake Processes. The group also studies the plant physiology looking for effects on plants due to atmospheric chemical components. The underlying questions are related to the extent in which lichens may reflect the element contents of particulate matter, which may possibly be dominated by its soluble element concentration fractions. This is the subject of one Ph.D. thesis and one project funded by FCT. Lichen dynamics, this is, accumulation and release are being deeply studied.

Nutrition. Selenium has been the target. A PhD thesis was finished and aimed to conclude on selenium in Portuguese diets. A project was now accepted for FCT financial support aiming to continue the study in cereals, supported by supplementation of the element and study of its absorption (how, how much) in the cereal pant and the cereal grains.

Training. The research unit has a strong component in post graduation training. An intensive workshop will take place at ITN on 2009, on the different expertises of the group. It will be available to any interested attendee from ITN and other Institutes/Universities. The group organizes international conferences.

Participation in intercomparison exercises Whenever offered, the group collaborates in data intercomparison, to improve data quality.

Services. Analytical services are also provided under request.

Research Team

Researchers

M. CARMO FREITAS, Princ. Res., Group Leader
S.M. ALMEIDA, Ciência 2007, FCT
H.M. DUNG, Post-doc., FCT grant; Ciência 2007, FCT
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A. HOSSAIN, Post-doc., FCT grant

Technical Personnel

I. DIONISIO, Laboratory assistant

Students

M.G. VENTURA, PhD student (finished June)
R. GODINHO, PhD student
S. SARMENTO, PhD student
B. VIEIRA, PhD student, FCT grant
A. CRUZ, PhD student
C. REPOLHO, FCT project fellow

Collaborators

A.M.G. PACHECO, Aux. Professor, CERENA/IST, Portugal
H.TH. WOLTERBEEK, Sen. Res., TUDelft, The Netherlands
M.M. FARINHA, ISQ, Portugal (on-going PhD)
A.P. MARQUES (PhD student, finished October)

Characterising Air Particulate Matter Composition and Sources for an Epidemiological Study

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Objectives

The project "Impact of Atmospheric Aerosol on Human Health" focuses on the chemical characterization of PM_{2.5} aerosols aiming to analyze the health risks associated with exposure to aerosols. It also aims to understand how their chemical composition contributes to the toxicity and the human health problems, usually associated with fine particles. The study of the associations between the sources contribution and the health impact aims to introduce focused abatement strategies in industrial processes, automobile circulation and city planning; they might contribute to the decrease of particulate levels and, consequently, the decrease of impact on human health.

Results

Thirty seven basic schools of Lisbon city followed a questionnaire about respiratory diseases, nutrition habits, ingested medication and environmental aspects, among others. The questioned children were 5 to 10 years old, and the answers were collected from June to December 2006. Results showed that from 1175 children inquired 25.9% had asthma and 27.7% had rhinitis.

Students from four schools around the air sampler (São José, São João de Brito, n° 183 and Actor do Vale) were selected and rhinitis and asthmatic symptoms were daily registered from May 2007 to April 2008.

In 2007, PM_{2.5} was collected in a daily basis in the centre of Lisbon. Sampling was done with a Partisol sampler using Teflon[®] filters. The filter loads were measured by gravimetry using a Mettler Toledo balance with 0.1 µg sensitivity. The exposed filters were cut into two parts controlled by weight: one was analyzed by Neutron Activation Analysis and the other was analyzed by Ion Exchange Chromatography. The irradiation was performed in the Portuguese Nuclear Reactor for 5-7 h, and measurements of 4-7 h after 3-7 days and 4 weeks of decay were made with high purity high resolution germanium detectors, with automatic sample changers. A comparator – 0.1% Au-Al disc – was irradiated and measured for application of the k_0 standardized neutron activation analysis.

PM_{2.5} annual average mass concentration was 19 µg/m³. Therefore, results show that the studied children, living and studying in Lisbon, are breathing an atmosphere with fine particles concentrations higher than advised by World Health Organization and U.S. Environmental Protection Agency, although below the proposed European Union value.

PM_{2.5} levels are mainly due to anthropogenic particles, being the ions SO₄²⁻, NH₄⁺ and NO₃⁻ the most abundant species in PM_{2.5} (Fig. 1). These ions derive from gas to particle conversion processes and are associated with anthropogenic sources such as traffic

and industry. The concentration variability along the day and the ratio between weekdays and Sundays show, as expected, that traffic is an important source of particles in Lisbon.

Higher number of rhinitis episodes were observed in April (123 children) and lower number in August (27 cases) in the Lisbon basic school inquired population. The questionnaires revealed that 56 of the children reporting rhinitis in April and August live in streets where trucks are passing frequently or the whole day. The children inhale higher concentrations of zinc and antimony in April than in August, mainly due to the high traffic reduction in August. Furthermore in April the studied anthropogenic elements are more concentrated in finer particles (PM₁ or lower) than in PM_{2.5}. Such small particles enter easily the lungs. Pollens were guessed not to interfere with the rhinitis cases found because in April only 18 children out of 123 showed hay fever and rhinitis together. The traffic by itself, with all its pollutant (inorganic+organic) charges, may then be the main cause for the higher number of rhinitis complains in April than in August. Back trajectory analysis showed that ocean contribution is very significant for PM_{2.5} collected in the centre of Lisbon. Maritime samples presented the lowest concentrations for SO₄²⁻, NH₄⁺ and NO₃⁻. This fact could be attributed to the transport of cleaner air masses from the sea and to the existence of better vertical dispersion conditions during these events.

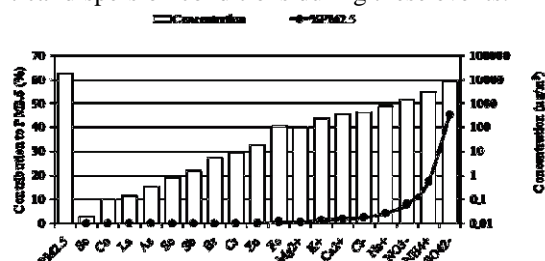


Fig. 1. a) Average concentration of PM_{2.5} species (ng/m³) and its contribution for total mass of PM_{2.5} (%). b) Average contribution of the aerosol species to PM_{2.5} mass.

Published work

M.C. Freitas, S.M. Almeida, A.M.G. Pacheco, I. Dionísio, C. Repolho, A. Caseiro, C.A. Pio, C. Alves (2008) Seasonal exposure to air pollutants characterisation for a respiratory epidemiological study, *Journal of Radioanalytical and Nuclear Chemistry* (accepted).

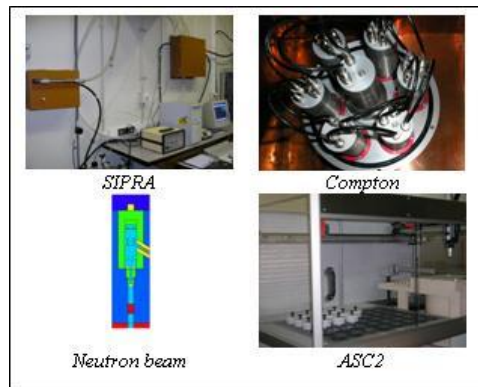
S.M. Almeida, M.C. Freitas, C. Repolho, I. Dionísio, H.M. Dung, C.A. Pio, A. Caseiro, A.M.G. Pacheco (2008) Characterizing air particulate matter composition and sources for an epidemiological study, *Journal of Radioanalytical and Nuclear Chemistry* (accepted).

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Neutron Activation Analysis at ITN

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The irradiation and count techniques of neutron activation analysis (NAA) includes 1) fast pneumatic irradiation facility (SIPRA) with epithermal or/and thermal neutrons upgraded; 2) Compton suppression system (CSS) with and without anti-Compton mode enabled and automatic sample changers (ASC2). The systems have been optimized and combined to determine multi-element in quartz and Teflon aerosol filters. The elemental concentrations resulted from the optimized and combined techniques of NAA for the elements: Al, As, Br, Ca, Cl, Co, Cr, Cu, Fe, Hf, I, K, La, Mg, Mo, Na, Sb, Sc, Si, Sm, Th, Ti, U, V, W and Zn. These elements have been used in source receptor modeling at sampling sites such as Azores, Aveiro and Lisbon. The k_0 -standardized method of NAA has been used for the

calculation of elemental concentrations in samples. The calibration of all gamma-ray spectrometers have been done each six months. The neutron spectrum parameters at irradiation facilities used for k_0 -NAA on the Portuguese research reactor have been re-characterized after changing fuels from HEU to LEU. Facilities for Prompt Gamma Neutron Activation Analysis (PGNAA) are being installed at the reactor. PGNAA permits the quantification of some elements undetectable by traditional NAA. At this stage we have planned the new facilities using the Monte Carlo code MCNPX to build a model of the proposed PGNAA facilities. These included thermalising the current epithermal beam by the introduction of a sapphire crystal into the beam line. The intercomparison runs by NAA with three “coffee” samples (Brazil), three tobacco samples (Poland) and two mussel samples (Brazil) have been completed. Several protocols and equipment have been documented and the non-conformance has also been managed following the ISO-17025 guidelines.

Exhaled Breath Condensate: a tool for noninvasive evaluation of pollutant exposition?

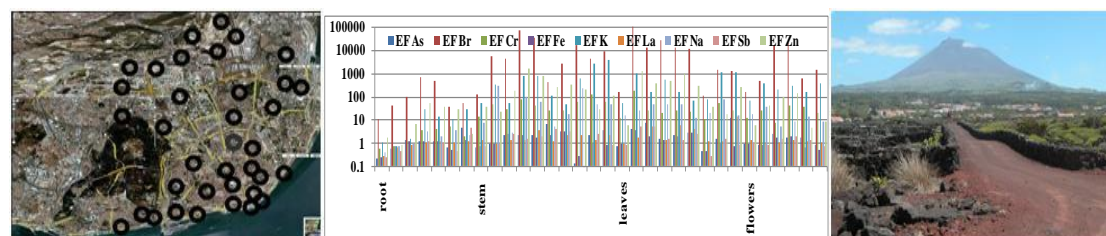
S.M. Almeida, T. Pinheiro, A. Bugalho de Almeida¹, S. Garcia², A. Barreiros³, M. F. Araújo, M. Santos, M.C. Freitas, L.C. Alves, P. Félix, C. Franco, B. Batista

The aim of the present study is to investigate whether Exhaled Breath Condensate (EBC) can be employed for a better risk assessment among humans exposed to toxic pollutants, in lead processing industries. The project is a joint initiative of ITN units UFA and URSN, together with the Instituto de Soldadura e Qualidade and the Hospital de Santa Maria. The primary objective is to develop a new non-invasive human bioindicator that could be applicable for professional exposition. During 2008 industries were selected and EBC sampling was tested in voluntaries to establish the better methodology to sample, store and analyse the EBC. Preliminary tests were also made in workers along the working shift to define the most representative sampling time. EBC chemical characterization are being performed by TXRF in INETI and by ICP-MS in ITN, the latter recently installed under the Programa Nacional de Re-Equipamento. This collaborative work with the Environmental and Analytical Chemistry Group of ITN and LAAQ/INETI will enable methodology validation and perform inter-laboratory exercise for analytical performance comparison.

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Different aspects of biomonitoring, epidemiology and data handling

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This study is the subject of 4 Ph.D. grants and 2 projects funded by FCT. It aims to map air pollution in Lisbon city by exposure of lichen and bark transplanted from clean areas to 22 school courtyards, and measurement of conductivity and determination of chemical element contents after being exposed. Also it aims to infer the remote air pollution in altitude by exposing lichens every 150 m starting at sea level to the summit of Pico Mountain, Azores, and analysing them for element contents. At São Domingos mine, vascular plants and soil were collected and analysed after separation of the plant in root, stem, leaves and flowers. Enrichment factors were determined showing higher enrichments in stems and leaves mainly for arsenic, bromine and antimony.

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