

# Applied Chemistry to the Earth and Environmental Sciences

## Introduction

The activities that have been developed by the research group called APPLIED CHEMISTRY TO THE EARTH AND ENVIRONMENTAL SCIENCES aim, in a broad sense, the study of the distribution and behaviour of chemical elements and isotopes in the fields of environment and earth sciences.

Some of the capabilities developed within this research group are rather unique, e.g. the neutron activation analysis (developed by this group in Portugal since the seventies) is based on the use of the nuclear research reactor (unique in the Iberian Peninsula) and the environmental isotopes laboratory (radiocarbon dating, tritium measurements and mass spectrometry of light elements) is also unique in Portugal. Environmental isotopes (C, O, H) have been applied to study and characterize present and ancient environments, namely in the fields of isotope hydrology, palaeoclimatology and palaeoceanography. Neutron activation analysis and X-ray fluorescence spectrometry combined with other techniques, in collaboration with researchers from other Institutions, have been applied in studies of pollution monitoring and modelling, sedimentary dynamics, cultural heritage and natural resources. As a consequence, these particular capabilities have led to an active engagement of the staff of this group in several research projects in partnership with national and international teams from Universities and Research Laboratories.

## Research Team

Researchers –	5	(4 PhD or equivalent)
Research Students –	7	
Undergraduate Students –	6	
Technicians –	3	

## Publications

Journals –	9	(4 in press)
Proceedings –	12	(3 in press)
Special Publ. –	1	
Internal Reports –	1	
Conf. Commun. –	12	
Theses:		
Lic. –	5	
MSc. –	2	

	10 <sup>3</sup> PTE
<b>Expenditure:</b>	<b>18.207</b>
Missions:	3.819
Others Expenses:	6.682
Hardware & Software:	2.806
Other Equipment:	4.900

		10 <sup>3</sup> PTE
<b>Funding:</b>		<b>18.207</b>
OE/ITN	OF	2.415 <sup>(1)</sup>
External	1996	2.134 <sup>(2)</sup>
Projects:	1997	13.394
Others		274

<sup>(1)</sup> This cost will be covered by external funding  
<sup>(2)</sup> Funding not used in 1996

## Chemical Composition of Sediments, Suspended Matter, River Water and Ground Water of the Nile (Aswan-Sohag traverse)

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### Abstract

Sediment, suspended matter, river water and ground water samples were collected at twelve sites in the drainage valley of the Nile River, around Sohag (Central Egypt) and close to the Aswan High Dam. Elemental composition of the river water (27 elements), ground water (8 elements), suspended matter (12 elements) and sediments (12 elements) was studied.

Aswan High Dam construction, agricultural and industrial human activities have led to dramatic changes in the Nile River chemistry. Nowadays, the Nile River has the highest dissolved salt content among the major African rivers. Dissolved transported is a major process for Ca, K, Sr, Zn, Cu, Ni and V. Manganese, Fe and Cr are mainly carried by suspended matter. The Nile suspended matter is exhausted in almost all elements studied (except for Mn) compared to the world average river suspended matter. Along the course of the river the distribution of elements in the suspended matter and sediments is generally controlled by natural processes: the relative importance of elemental transport phases; and the oxidation, precipitation and sedimentation of mineral species through the varying physico-chemical conditions of the environment. Pollution input in the Nile particulate load is not major as compared to the natural inputs. Eight genetic particle types describe the composition of the Nile suspended matter and sediments: 1) biogenous-aeolian (or silica); 2) terrigenous (Fe-aluminosilicate); 3) authigenic (calcium carbonate); 4) biogenous (apatite); 5) authigenous-terrigenous (Fe-oxyhydroxide-montmorillonite); 6) diagenetic (iron-sulfide); 7) terrigenous (titanium oxide); 8) authigenous (Mn-Fe-oxyhydroxide).

*The Science of the Total Environment* **201** (1997) 195.

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## Detrital Chromite in the Serra Alta (South Portugal) Quartzites: Chemical and Structural Characterization and Geological Implications

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### Abstract

Several quartzite bodies outcrop along the Ferreira-Ficalho Thrust Fault (South Portugal), a major accident of the Iberian Variscan Orogen. The sediment is a very pure quartz sandstone, with trace amounts of ultra-resistant heavy minerals and chromite. Its age is not well known, but is younger than the first phase of deformation, essentially a Westfalian event. Chemical characterization (microprobe analyses and Mössbauer spectroscopy) showed the chromite to be unique: Besides being Zn-rich, complexly zoned and a cation deficient spinel, all the iron

was found to be fully oxidized to Fe<sup>3+</sup>. Structure refinement of single-crystal X-ray diffraction intensities unambiguously identifies the mineral as a chromite and the hyperfine parameters estimated from the Mössbauer spectra are consistent with tetrahedrally coordinated Fe<sup>3+</sup> in the spinel structure. Current geodynamical models see the Ferreira-Ficalho Thrust Fault as a first order suture resulting from a complex collision of two distinct continental blocks with partial obduction of the intervening oceanic crust. The chromite grains of the quartzites could be envisaged as remnants of an early erosion of this obducted oceanic crust, but its unique chemical character does not allow any definite conclusion. Yet, the complete quartzite heavy mineral contents and its petrographic features are not consistent with their deposition within a continental collision situation.

*Mineralogical Magazine* **61** (1997) 627-638.

## **Bioaccumulation of Heavy Metals using *Parmelia sulcata* and *Parmelia caperata* for Air Pollution Studies**

**M.C. Freitas, A.S. Nobre**

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### **Abstract**

k<sub>0</sub>-Standardized INAA was applied in this work to the elemental determination in two lichen varieties of the species *Parmelia caperata* and *sulcata*. The aim was to find out differentiations between the two varieties concerning the accumulation of elements, namely heavy metals, from the air. The samples were collected at about 70 locations randomly chosen in the whole country (Portugal). It was found a similar local variation for both species, between 20 - 25 %. From the comparison it was observed that *Parmelia sulcata* accumulates larger amounts of most of the elements determined than *Parmelia caperata*; only Ca is more accumulated by the *caperata* and Hg are similarly absorbed by both varieties. Therefore it was concluded that *Parmelia sulcata* should be preferred as bioaccumulator when both varieties are present. Some pollution sources were identified, but the sampling net was too short to obtain an exhaustive identification. The quality control was made using NIST and IAEA reference materials: an accuracy of ± 10 % was found. The precision has also been estimated: it is better than 11 % except for Hg (15 %), Sr (13 %), Ti (19 %) and Mg (32 %).

*Journal of Radioanalytical Nuclear Chemistry, Articles*, **Vol. 217** No.1 (1997) 17-20.

## **Monitoring of Trace-Element Air Pollution in Portugal: Qualitative Survey**

**M.C. Freitas<sup>\*</sup>, M.A. Reis<sup>\*\*</sup>, L.C. Alves<sup>\*\*</sup>, H.Th. Wolterbeek<sup>\*\*\*</sup>, T. Verburg<sup>\*\*\*</sup>, M.A. Gouveia<sup>\*</sup>**

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### **Abstract**

During the months of and August 1993 a lichen collection campaign was held in Portugal where about 250 samples were collected and analysed by thick target TPIXE and INAA. Results for 44 different elements were obtained and a data base was built and subjected to

Monte Carlo Aided Target Transform Factor Analysis (MTATTFA), method developed at IRI (Delft). 10x10 km Coast and 50x50 km far from coast sampling grids were used for collection, concentration data as well as factor patterns were extrapolated to the whole country making use of an extinction rule of  $1/r^3$ . In this work we will present the results which were obtained based on a reduced data set of 36 elements measured by INAA. The results for 22 elements obtained by TTPIXE were published elsewhere. In this work we will also present the conclusions considering all the elements determined by both techniques, concerning 44 elements.

*Journal of Radioanalytical Nuclear Chemistry, Articles, Vol. 217 No.1 (1997) 21-30.*

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## **Chemical Composition of Sediments and Suspended Matter from the Cauvery and Brahmaputra Rivers (India)**

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### **Abstract**

Suspended matter, surface and core sediments from the Cauvery river and core sediments from the Brahmaputra river were analysed (15 elements) by the energy-dispersive X-ray fluorescence technique.

The Cauvery river load indicates a relative predominance of solute *vs* suspended transport. Cauvery river suspended matter is depleted in Al and Si, and enriched in Ca, Mn, Cr, Ni, Cu, Zn and Sr relative to the world's average suspended matter. As the sampling web covered largely the Cauvery delta, the enhanced heavy metal concentrations in the suspended matter are explainable in terms of chemical-physical processes in the zone of mixing. Flocculation of the dissolved metal species causes their transformation in the suspended state. Consequently, deltal suspended matter is richer by 1-2 orders of magnitude in heavy metals than the main river course background.

Cauvery surface sediments reflect the Indian average sediment composition. They have a homogenous composition along the river course and a heavy metal content that is lower than the one in the Cauvery suspended matter.

Sedimentation rates in the Cauvery and Brahmaputra are comparable with those published for other Indian rivers. The sediment flux to the Brahmaputra bed is higher than for the Cauvery. Mass accumulation rates for heavy metals in the sediments were determined. It is supposed that the large and synchronous fluctuations in the temporal distribution of the heavy metal accumulation rates have been caused by cyclic climatic changes over the Indian sub-continent. An additional supply of transition elements, due to the urbanization and industrial activities, could be assumed to cause the enrichment in the uppermost core layers.

*The Science of the Total Environment* **212** (1997) 89.

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## **Elemental Composition in Sediments and Water in the Trancão River Basin. A Preliminary Study**

**F. Araújo, T. Pinheiro, L.C. Alves, P. Valério, F. Gaspar and J. Alves**

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### **Abstract**

The Trancão river basin, located in the Lisbon area shows preoccupying pollution levels, that constitute a threat to public health and the ecological system. This work reports on the results obtained in the analysis of surface sediments (EDXRF) and water (PIXE) collected in the wet and dry season during 1996.

In general, bulk sediments and water show high concentration levels for some heavy metals like Cr, Cu, Zn and Pb. The elemental contents variation of samples collected at the different sites of the river basin were large, owing apparently to pollution sources, seasonal variabilities and grain size distribution (sediments). In the dry season, effluents (industrial and domestic) showed a stronger influence on the sediment composition. High levels of As and Br were found in the water that can be attributed to extended sources like sewage sludge and fertilizers. In some locations, the metals, Ca and organic matter enrichment could be associated with a paper mill and metal processing industry (high levels of Cr). At the estuary, the decrease of metal content determined in the sampled water indicates the flocculation of dissolved organic and inorganic materials. However, no effects were found for the surface sediment metal content, probably due to a dilution with materials from the Tagus inner estuary (the largest in Portugal).

*Nucl. Instrum. Methods*, (in press).

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## **REE Distribution in Fine-Grained Sediments from the Portuguese Atlantic Shelf**

**MF Araújo & MA Gouveia**

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### **Abstract**

The importance of the trace element geochemistry, particularly the REE distribution has been recognized to be an important tool to characterize the origin of sediments and the corresponding sedimentation processes. REE have been determined in sediments collected at two fine silt-clayed deposits located at the Northwestern Portuguese shelf and at the main estuaries that drain the adjacent coastal area. We are discussing the shelf sediments to assess terrigenous input pattern of REE. The shale-normalized patterns seem to indicate distinct pathways of the different river borne materials when related with the fine sediments deposited at the shelf. Therefore, while for the system Douro estuary/silt-clayed deposit, these patterns are identical, in the case of the system Minho estuary/silt-clayed deposit, a relation between the river borne materials and the deposited sediments can not be established.

*Water Rock Interaction WRI-9 Conference Proceedings* (in press).

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## **Geochemical Signatures of Main West Atlantique European Estuaries in the Mud Fields of the Shelf. Examples of Tagus, Douro, Minho and Gironde**

**Fátima Araújo<sup>1</sup>, Jean-Marie Jouanneau<sup>2</sup>, Pedro Valério<sup>1</sup>, Paula Paiva<sup>1</sup>, Ângela Gouveia<sup>1</sup>, Olivier Weber<sup>2</sup> and João M.A. Dias<sup>3</sup>**

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### **Abstract**

The Western European Atlantic continental margin (Portuguese margin and Gulf of Biscay) constitutes a high energy area where fine-grained deposits are in general well circumscribed and situated in face of the main estuaries.

The origin of these silt-clayed formations has been established to be more recent than it had been previously envisaged (Lesueur, 1992; Drago, 1995). Furthermore, some studies seem to prove that these complexes are still active formations (Jouanneau and Weber, 1989a; Weber *et al.*, 1991; Araújo *et al.*, 1994).

In these conditions can one recognize, based on the trace element distribution and the geochemical pattern of the deposits, that the origin of these complexes is directly related with the sediments exported from those estuaries? Besides, in what extension the transfer process modifies the pattern? Finally, is there any record of recent human activities?

This study has been therefore focused on the geochemical analysis (EDXRF, INAA and AAS) of superficial sediments collected at these complexes and compared with fine-grained sediments from the main estuaries.

Apparently, it seems that the large estuaries are the main sources of the current fine sedimentation in the mud patches of Tagus, Douro and West-Gironde. Besides, the transport of these materials does not influence the geochemical pattern of the transported sediments. An exception is probably occurring at the mud field in front of the Minho estuary that seem to show a multiple origin, where it is reasonable to predict a complementary contribution from the Galician rias.

Submitted to *Oceanologica Acta*

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## **Elemental Composition of Demospongiae from the Eastern Atlantic - Coastal and Deep Sea Waters**

**M. Fátima Araújo<sup>1</sup>, Alexandra Cruz<sup>2</sup>, Madalena Humanes<sup>2</sup>, Maria Teresa Lopes<sup>2</sup>, José Armando L. da Silva<sup>3</sup>, J.J.R. Fraústo da Silva<sup>3</sup>**

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### **Abstract**

The elemental composition (Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Zr and Pb) of 32 coastal and deep-sea Demospongiae, belonging to different species and collected along the eastern Atlantic Ocean and in the coast of western Europe (Portugal and Madeira island) and Africa (Angola), has been determined by energy-dispersive X-ray fluorescence spectrometry (EDXRF):

In some species it has been observed a selective accumulation of particular elements, unrelated to sampling location. This was the case of nickel which is accumulated to a considerable extent

by *Suberites carnosus* specimens and of zinc which distinguishes *Hymeniacidon sanguinea* (zinc accumulation) from *Halichondria panicea* species, both of the Halichondria order. Very high levels of bromine were also observed, particularly in the non-siliceous sponges. Limitations of the analytical results of sponges, given the possibility of extensive contamination with foreign particles, fine-grained sediments, as well as association with other macro- and micro-organisms, prevent a thorough statistical treatment of the data obtained. Nevertheless good correlations were observed between the concentration of several elements, for example zinc and bromine in the Halichondria sponges, and, as expected, between elements which have no known biological function and must derive from uptake of geological materials, e.g., Ti, Cr and Zr. Silicon, of course, is the dominant element, varying between 1% and 33% (dry weight) of sponges.

Submitted to *Oceanologica Acta*

## Elemental Composition and Enzyme Activity in Demospongiae

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### Abstract

The elemental composition of several coastal and deep-sea Demospongiae, belonging to different species and collected along the eastern Atlantic Ocean, in the coast of western Europe (Portugal and Madeira island) and Africa (Angola) has been determined by energy-dispersive X-ray fluorescence spectrometry (EDXRF). In some species it has been observed a selective enhanced accumulation of particular elements, unrelated to sampling location. Several of these elements are found in the active center of some enzymes and it seemed of interest to relate their presence to particular aspects of the metabolism of the corresponding sponges, although the possibility of extensive contamination with foreign particles, fine-grained sediments as well as association with other macro- and micro-organisms can not be excluded for these filter feeding organisms.

The very high levels of bromine, observed particularly in non-siliceous sponges, prompted us to search for the eventual presence of haloperoxidase activity in these organisms. In effect, two bromoperoxidases from a tropical marine sponge have already been isolated, but the nature of their activity center has not yet been ascertained.

Furthermore, catalase and superoxide dismutase activities were also found in crude extracts of some sponges examined.

Communication to: "European Research Conference in Chemistry of Metals in Biological Systems", Tomar, Portugal, 7-11 May 1997.

## Rare Earth Elements Geochemistry Applied to Provenance and Alteration Processes of Granitic Rocks in Megalithic Monuments

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### **Abstract**

REE patterns were used for provenance studies of two granitic dolmens of Alentejo, Portugal. The results obtained suggest that these elements are good fingerprints to identify monuments stones origin despite the small size of the samples collected in the dolmens. The majority of the stones of Zambujeiro and Tapadão dolmens are local. REE data also showed that the alteration processes and the degree of alteration depend on the environmental conditions of the monument since their construction.

*Proceedings of the IV<sup>th</sup> International Symposium on the Conservation of Monuments in the Mediterranean Basin, Vol.1, p.247-252, 1997.*

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## **Determination of Rare Earth Elements in Geological Samples: A Comparative Study of Instrumental Neutron Activation Analysis and Inductively Coupled Plasma Mass Spectrometry**

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### **Abstract**

Rare earth elements (REE) – La, Ce, Nd, Sm, Eu, Tb, Yb and Lu have been determined by instrumental neutron activation analysis (INAA) and inductively coupled plasma-mass spectrometry (ICP-MS) in twenty geological reference materials. These analyses allow the assessment of the precision and accuracy of the methods. In general, very good to good precision is attained by INAA. Higher uncertainty is achieved by ICP-MS mainly for elements with very low contents, occurring as about ten times chondrite values. Supported by statistical basis, systematic, both constant and/or proportional errors are found for Lu by INAA and for Nd, Sm, Eu and Tb by ICP-MS. It seems that analytical and sampling errors may affect the accuracy of both methods, with more incidence on ICP-MS. Interferences due to matrix effects, drift, memory effects, inadequate blank corrections or calibration are often not easily detected or overcome. Nevertheless if a careful control of the analytical and instrumental conditions is followed, both methods are quite suitable for the REE contents determination in samples ranging in a wide geological composition.

Submitted for publication.

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## **Trace Elements in Residual and Sedimentary Deposits of Kaolins from Minho (Nw Portugal)**

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### Abstract

Residual and sedimentary deposits of kaolins exploited nowadays from the northwestern part of Portugal were studied. Mineralogical and chemical analyses of whole samples and the respective < 2 (m fractions were made by X-ray diffraction and instrumental neutron activation analysis, with a view to characterize and differentiate both types of kaolin deposits.

The residual kaolins are in general richer in K, Rb and Cs, which is in agreement with higher proportions of alkali feldspars and micas. The sedimentary kaolines are richer in clay minerals, with a high content of kaolinite, which is associated with higher concentrations of trace elements namely rare earth elements (REE), Sc, Cr, Co and Th.

The distribution of the elements analysed in the < 2 (m fraction relative to the whole samples are significantly different in the two types of deposits. In general the elements are more uniformly distributed in the fine fraction of the sedimentary deposits. The REE are enriched in the residual deposits with a relative concentration of the intermediate REE, while Eu is concentrated during the sedimentary processes.

*Seventh Annual V.M. Goldschmidt Conference*, Tucson, Arizona, USA, Abstracts, p. 167, 1997.

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## Geoquímica Aplicada à Caracterização e Identificação da Cerâmica Arqueológica Romana “Bracarense”

*F. Oliveira<sup>1</sup>, M.I. Prudêncio<sup>2</sup>, M. Martins<sup>3</sup>, M.A. Gouveia<sup>2</sup>, M.A. Sequeira Braga<sup>4</sup> & M. Delgado<sup>3</sup>*

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<sup>3</sup> Unidade de Arqueologia, Universidade do Minho, Braga, Portugal

<sup>4</sup> Dep. Ciências da Terra, Universidade do Minho, Braga, Portugal

### Abstract

Chemical and mineralogical analyses of “bracarense” pottery sherds from roman settlements of the north of Portugal and Galiza (Spain), as well as other types of ceramics, have shown that “bracarense” ceramics found in Braga and Aquis Querquennis, differs from the local ceramics.

A comparative study between ceramics and clays collected from Chaves to the coast region showed that “bracarense” ceramics most probably was not made near Braga. The clay or clays sources of this type of ceramics seem to be kaolin type as those found in Barqueiros.

*Proceedings of the X Semana de Geoquímica e IV Congresso de Geoquímica dos Países de Língua Portuguesa*, pp. 617-620, 1997.

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## Redistribuição de Elementos Traço Associada à Transformação dos Estado do Ferro num Paleossolo em Formações Ferralíticas Terciárias

*M.I. Prudêncio<sup>1</sup>, M.A. Sequeira Braga<sup>2</sup>, J.C. Waerenborgh<sup>1</sup> & M.A. Gouveia<sup>1</sup>*

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### Abstract

A pelesoil developed in Tertiary deposits (NW Portugal) with a zone of columnar pedogenetic structures showing strong color variations and the presence of milimetric black nodules was studied. It was found that the color change is associated with the iron forms – in the red parts only hematite occurs while in the yellow part only poorly crystallized goethite is detected. White/gray structures correspond to deferrated zones. The small black nodules result from the precipitation of hollandite and pyrolusite among quartz, kaolinite and mica grains. Fe, As and U are strongly correlated and the REE are concentrated in the white zones during these Fe reduction/oxidation phenomena.

*Proceedings of the X Semana de Geoquímica e IV Congresso de Geoquímica dos Países de Língua Portuguesa*, p. 303-306, 1997.

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### Degradation Processes of Trachytes in Monument Façades (Azores, Portugal)

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### Abstract

Petrographic, mineralogical and chemical analyses confirmed the provenance of the stones used as building materials of the main façade of the Ribeira Grande church (Azores, Portugal). In spite of the serious state of decay of the monument stones most of the chemical differences found seem to be partially inherited from the quarry. However a significant increase in the CaO content in the monument stones is observed certainly due to the use of mortars, cements and lime as building or restoration materials. A depletion of Eu is also found in those samples probably due to preferential dissolution of plagioclase. A major difference between the quarry and monument environments is deduced from the study of the Fe forms. A much higher oxidation degree is observed in the samples from the church stones (where Fe is mainly present as (Fe<sub>2</sub>O<sub>3</sub>)) as compared to any of the rock samples including the most weathered ones.

*Water-Rock Interaction WRI-9 Symposium Conference Proceedings* (in press).

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## Soil Versus Lichen Analysis on Elemental Dispersion Studies (North of Portugal)

*M.I. Prudêncio, M.A. Gouveia, M.C. Freitas, M.A. Reis, L.C. Alves and L. Chaves*

*ITN- Instituto Tecnológico e Nuclear, EN 10, 2685 Sacavém, Portugal*

### Abstract

Chemical elements contents in topsoil and lichens sampled at regular intervals in the north of Portugal were obtained by using both comparative and  $K_0$  methods of instrumental neutron activation analysis. The topsoil chemical composition was studied in an attempt to discriminate between natural background and anthropogenic inputs, as well as to eliminate the influence of soil on the lichen composition. Topsoil maps revealed the existence of areas with anomalous concentrations due: (1) to natural causes (inherited from the initial rock) especially Cr in Trás-os-Montes) and (2) anthropogenic influence, namely Aveiro-Estarreja area for Cr and Co associated to high values of Fe. Br contents in topsoil decrease from the coast to the interior explained by the sea influence (wet deposition). Exceptional concentration values of As, Zn and W were found in one particular topsoil (Nogueira do Cravo), probably due to aerial inputs originated in mining activities. The enrichment factors (E.F.) in *Parmelia sulcata* relative to topsoil clearly showed that lichens are fingerprints of atmospheric pollution, especially for Cr, Zn, As, Br, Sb and W. The following areas with anomalous E.F. in lichens were detected: (1) Viana do Castelo – Braga for Cr, Sb, (Zn and Br), (2) Trás-os-Montes for Br, (3) Porto for As and Zn and (4) Aveiro-Estarreja for As, Cr, Sb and W.

*BioMap - International Workshop on Biomonitoring of Atmospheric Pollution, Abstracts, p. 3.5, Lisbon, Portugal, 1997.*

## $\delta^{13}\text{C}$ as a Tracer in the Origin of $\text{CO}_2$ in the Gaso-carbonic Cold Waters of Vilarelho da Raia, Vidago and Pedras Salgadas

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### Abstract

Several hot (Chaves) and cold (Vilarelho da Raia/Vidago/Pedras Salgadas)  $\text{CO}_2$ -rich mineral waters are present in an area of approximately 800 km<sup>2</sup> in the northern part of the country. On the basis of the thermal, isotopic and chemical characteristics of these waters, it was concluded that the  $\text{CO}_2$ -rich waters might represent meteoric waters which have been subjected to shallow depths in the bedrock. The chemistry of these waters seems to be strongly related to their gaseous phases, which consist of almost pure  $\text{CO}_2$ . The  $\delta^{13}\text{C}$  values, measured in the total dissolved inorganic carbon (TIDC), indicate a deep-seated (mantle) origin for the  $\text{CO}_2$ .

*Actas X Semana de Geoquímica / IV Congresso de Geoquímica dos Países de Língua Portuguesa. Braga, Portugal (1997) pp 571-574.*

## **Application of Geochemical and Isotope Methods in the Hydrodynamic Interpretation of the S.Mamede Carbonate Aquifer (Castelo de Vide)**

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### **Abstract**

This paper contains some preliminary results obtained in the research program “Aplicação de Métodos Geoquímicos Isotópicos e Modelos de Escoamento ao Aquífero Carbonatado da Serra de S. Mamede” (Projecto Nº PEAM/SEL/557/95). The financial support are supplied by JNICT. The results obtained are useful in the definition of the water quality and characterization of hydrochemical processes. However we present the particular aspects related with the contribution of the geochemical and isotopic methods to the hydrodynamic characterization of the aquifer.

I Congreso Ibérico de Geoquímica. VII Congreso de Geoquímica de España. Soria, Espanha (1997), pp 544-551.

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## **Use of Environmental Isotopes in the Study of the Aquifers Systems from Maciço das Setes Cidades (Azores) - Preliminary Results**

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### **Abstract**

The results obtained with the isotope analyses ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) performed in groundwater samples collected in springs, wells, in a lake and two lakelets at Sete Cidades Massif (Azores), allow the identification of a mixing mechanism between surface water and groundwater. In view of these results there is also the possibility of recharge of the aquifers systems by fog that surrounds the island approximately during all the year.

The springs located near the coastline, at low altitude, have a residence time in the order of 5 to 10 years based in the tritium content. The  $^3\text{H}$  values stands for a recharge area located relatively far away from the outlet.

Revista da Associação Portuguesa dos Recursos Hídricos (APRH) (in press).

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## **Multielement Analysis of Animal Tissues and Bones by Instrumental Neutron Activation Analysis**

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### **Abstract**

Recently we have applied to a project which aims to study paleodiets. One of the type of samples to be dealt with is human bones. Enough of these samples are available at University of Coimbra (Portugal). Up to now our group has not experienced the analysis by INAA of such samples. In this work, INAA of two standards of animal tissues and one of animal bone are presented in order to validate the analysis of the human bones. The standards considered are the IAEA animal muscle H-4, the IAEA animal bone H-5 and the NIST 1577a Bovine liver. These three standards cover a reasonable range of concentrations in several elements. Results are also presented for human bones of the paleolithic age. Different treatments are made to the samples in order to ease the preparation of the material for analysis, which may have implications on loss or contamination of elements. These losses or contaminations are studied in order to optimize the sample preparation.

Communication to: *BERM-7, Antwerp, Belgium, 1997.*

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## **Air Pollution on Heavy Metals and other Elements in Portugal**

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### **Abstract**

ITN is dealing with air pollution studies concerning heavy metals and other elements in Portugal, since 1992. The studies done led to the first reference data base of elemental air pollution in the whole country with identification of pollution sources. Lichens were used as biomonitors; eight antropogenic pollution sources were identified and correlated with the mapping of higher concentrations. A similar work was done using olivetree barks as biomonitors. Olivetree barks were collected within a grid of 10x10 km at the atlantic coast 200 km north and south Lisbon. The samples were analysed by instrumental neutron activation analysis for short and long lived nuclides. The results obtained for both lichen and bark were compared in terms of enrichment factors. We concluded that both biomonitors lead to similar conclusions in what air pollution is concerned.

Accepted for publication in the Proceedings: *Element Cycling in the Environment*, Warsaw, Poland, 1997.

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## Instrumental Neutron Activation Analysis in Air Pollution Studies

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### Abstract

Air pollution studies are being done routinely since 1990 at the Instituto Tecnológico e Nuclear (ITN, formerly ICEN/INETI).  $k_0$ -standardized instrumental neutron activation analysis ( $k_0$ INAA) and proton induced X-rays emission (PIXE) have been the analytical techniques used. Applications include analysis of air particulate matter having as support paper or polycarbonate filters, underground and rain water, lichens and other biomomitors.  $k_0$ INAA is very sensitive on these applications, even in filters where the blank has to be subtracted together with the irradiation container. Furthermore, small amounts of residuum coming from liophilization of waters such as 50 mg are enough to have concentrations for more than 20 elements. Concerning lichens and other biomonitors, large amounts such as 500 mg can be analysed avoiding the need for intense homogeneization of the material. Nevertheless, for air pollution studies, an important pollutant can not be determined by this technique, the lead. In this work, we shall present some results obtained on projects going on or just finished aiming to evaluate the air pollution in Portugal. We shall foccus in explaining how a large amount of samples can be dealt per month.

Communication to: *MARC-IV, Kona-Kailua, Hawaii, USA, 1997.*

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## Heavy Metals in the Atmospheric Environment

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### Abstract

Our Institute is dealing with air pollution studies in Portugal concerning heavy metals and other elements, since 1992. The techniques used have been INAA (Instrumental Neutron Activation Analysis), PIXE (Proton Induced X-Ray Emission) and ICP/MS (Ion Coupled Plasma Mass Spectrometry). With these techniques concentrations for about 30 elements can be determined, including all the heavy metals of interest in the environment. Samples of air particulate matter, lichen *Parmelia sulcata* transplants and rain water were monthly collected for 1 year at 6 locations (one reference location and 5 locations in the neighborhood of coal or fueloil power stations). The Gent PM-10 air sampler was used in collection of air particulate matter. This air sampler works with one fine filter (0.4  $\mu\text{m}$ ) and one coarse filter (8  $\mu\text{m}$ ), the air particles are then separated in two fractions: <2  $\mu\text{m}$  and the other one between 2  $\mu\text{m}$  and 10  $\mu\text{m}$ . Each filter, weekly collected, was divided for analysis: one half for INAA and one fourth for PIXE. Rain water was evaporated to dryness under infrared lamp, the residuum was acid digested with ultrapure acids (HF included) and analysed by ICP/MS. Lichen samples were washed in diionized water for 30 sec., ground in a Teflon mill, pelletized and analysed by PIXE and INAA. Mathematic models were defined to describe the response of the lichen transplants to the heavy metal availability in the atmosphere. Good correlations were found between elemental accumulation in lichens and elemental amounts in air particulate matter and rain water. The mathematical models are applied to the results obtained in a survey made to the whole country on July and August of 1993. This survey was obtained by picking up the lichen *Parmelia sulcata* in a grid of 10km x 10km along the portuguese western coast and 50km x

50 km in the interior of the country. As is well known surveys give qualitative information only; now, with the defined mathematical models, it is possible to quantify the survey. Therefore quantitative amounts of heavy metals and other elements in the atmosphere may be obtained for the whole country, at the time of the lichen sampling (July and August 1993). This work opens great perspectives to the biomonitoring applications. This work was made in collaboration with the International Atomic Energy Agency and Electricity of Portugal.

Communication to: *AOAC Annual Meeting*, San Diego, USA, 1997.

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## **Use of $k_0$ -Standardization Method at the Hahn-Meitner-Institut: a Way to Extend INAA to Environmental Samples for Multielement Determination**

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### **Abstract**

In order to extend INAA to environmental samples for multielement determination, the  $k_0$ -standardization method was implemented at the Hahn-Meitner-Institut. Differences on thermal neutron fluxes in the irradiation containers were found to be less than 6%, for both horizontal and vertical lines. Three irradiation channels were chosen: TBR, for short-lived nuclides; DBVR, for short- and medium-lived nuclides; and DBVK, for long-lived nuclides. Values for the deviation to the 1/E law and the thermal to epithermal ratio were determined for the three channels. The  $k_0$ -method was implemented in one Canberra detector which is moved towards the sample. Results obtained for reference materials are compared with (i) reference values, and (ii) values obtained via relative method. Reference materials were measured at the closest distance and at the reference distance: the results are also compared.

*2<sup>nd</sup> International  $k_0$ -Users Workshop Proceedings*, pág. 152, Março de 1997, Ljubljana, Slovenia.

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## **Monitoring of Trace Element Air Pollution at a Rural Site: Comparison with Results Obtained at an Urban Site**

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### **Abstract**

The Gent PM10 air sampler equipped with NILU stacked filter units (using 0.4 $\mu$ m and 8 $\mu$ m thick filters), was installed at the rural site of Tapada do Outeiro. The aerosols are being collected since August 1995 each week 16 h/weekend day and 16 h/midweek day: the 16 h are spread in 40 min. out of each hour for each 24 h period. One half of each filter was analysed by INAA, after being pressed into polyethylene containers. The  $k_0$ -method was used, wires of

IRMM 0.1% Au-Al being the comparator. It was observed that the antropogenic elements Zn, Sb, As, Se, and Hg are more concentrated in the fine filters, while the lithophilic ones concentrate better in the coarse filters. Enrichment factors were determined relative to Fe and based in Mason data. Several elements are enriched in both fine and coarse filters, namely Br, Zn, As, Se, and Sb. It was observed that Fe, As, and Br are more enriched at the urban site than at the rural site, as well as Hg, Zn, Sb, and Na. The quality control was performed using IAEA AIR-3/1 and NIST Urban Particulate Matter.

2<sup>nd</sup> International  $k_0$ -Users Workshop Proceedings, pág. 115, Março de 1997, Ljubljana, Slovenia.

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## Comparing Biomonitors Behaviour in Air Pollution Studies

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### Abstract

Our Institute is dealing with atmospheric pollution studies concerning heavy metals and other elements in Portugal since 1992. A few papers on this conference deal with results obtained during these studies. The general aims were to make a survey based on lichen *Parmelia sulcata* in a first step; secondly to define lichen *Parmelia sulcata* time response models to environmental elemental availability in order to quantify the survey. On the course of these studies, we also sampled other biomonitors other than *Parmelia sulcata*, namely *Parmelia caperata* in one third of the locations and olive tree stems in all the locations (as support of the lichens used for the survey). Other monitor, not biological one, was the soil which we have collected in all the locations used for the survey (this is dealt with in other paper presented at this workshop). In this work, comparison between results obtained with *Parmelia sulcata*, *Parmelia caperata* and olive tree stems is made. Comparing the results obtained via both *Parmelia*, we conclude that *P. sulcata* is a better accumulator for all the elements studied, except for Ca, for which *P. caperata* is better and Hg, for which both accumulate similarly. This work was made with support of IAEA.

Communication to: *BioMAP*, Lisboa, 1997.

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## Heavy Metal Contents in Polymers Used in Food Packing

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### Abstract

The polymer industry in European Union leads with more than 60 chemical elements in polymer material, in concentration ranges within the ppb and % levels. These elements are mainly the consequence of the use of additives and catalisators during their production. The EU rule EC-Directive 94/62/EC refers the limits fixed for the heavy metal contents in Cd, Cr,

Hg and Pb in plastic packages. For becoming this rule effective it is necessary to have available reference materials in the market for quality assurance. Therefore a project started aiming to prepare and to certify two polymeric elemental reference materials with different heavy metal contents. In this work, preliminary results obtained on this certification are shown. It is also presented results for heavy metals in plastic currently used in food packing, in order to evaluate the proximity of their contents to the legislation. INAA was used as analytical technique.

*Proceedings of 3<sup>rd</sup> Meeting on Chemistry of Food*, pp.. 273-275, March 1997, Faro, Portugal (in portuguese).

## **Palaeoclimatic and Palaeodynamic Characterization of the Aveiro Cretaceous Multiaquifer Trough the Application of Environmental Isotopes**

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### **Abstract**

Through the application of isotope and hydrochemical techniques in the study of Cretaceous multiaquifer system of the Lower Vouga Basin, we try to evaluate the effect of the high exploitation of groundwater of this system along the last 4 decades.

Between km 5 and 8 the <sup>14</sup>C content of the groundwater decrease almost linearly with the increasing distance, along the general direction of groundwater flow. However, between km 8 and 16 the concentration of <sup>14</sup>C remains almost constant, indicating a much higher apparent flow velocity of groundwater, resulting from intense flushing of the aquifer during the last glacial period about 18 ka . This flushing was induced by the decrease in the sea level by about 100 m.

On the other hand, an enrichment in <sup>18</sup>O and in <sup>2</sup>H downgradient from the recharge area can be observed along the flow paths, with more positive δ values for higher apparent <sup>14</sup>C ages. This apparent enrichment in heavy isotopes observed for Aveiro palaeowaters is unique in the European continent, and probably reflects the fact that the global ocean was enriched in both <sup>18</sup>O and <sup>2</sup>H during the glacial period.

Noble gas determinations (He, Ne, Ar, Kr and Xe) as a palaeoclimatic indicators were carried out on these waters. The palaeotemperature results (groundwater with Pleistocene ages) give an average temperature of 5°C lower than the water samples collected either in the shallow system or in the deep aquifer zone with Holocene ages.

Accepted for presentation and publication in the proceedings of 4° Congresso da Água. “A Água Como Recurso Estruturante do Desenvolvimento”. Lisboa, Portugal (1998).