



## Book of Abstracts



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**Keynote Lecture**

Ignasi Queralt (CSIC-Spain)

<http://eventos.fct.unl.pt/heavymetals2016/>

## Visualizing the interactions of nanoparticles with cells

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The exponential production and use of manufactured nanoparticles (NPs) lead to an increase in the concern about their toxicological effects in the environment, 'non-target' organisms and human health. The foundation behind NPs cellular effects relate to increased reactivity resulting from their small size and the large number of surface atoms compared to their bulk counterparts. However, how different NPs interact with cells and modulate their response are challenging issues, which require the development of efficient models and screening methods. Understated issues are quantization, transport into cells, and resolving nanoscale particles in the whole cell volume. A few approaches have been recently reported, such as correlative microscopy by using optical techniques and transmission electron microscopy in tandem, super-resolution and confocal microscopy. Some of these methods are laborious and complex in terms of instrumentation and sample preparation and others require modification of native NPs to fluorescently labeling them. Ideally, new imaging techniques will be developed to visualize and quantify local populations of NPs at nanometre resolution, in real time within cells without structural damage. This is in fact the prospect held by nuclear microscopy techniques based on focused MeV ion beams. Recent developments brought ion beam techniques to a privileged and top position concerning bioimaging by enabling tens of nanometer spatial resolutions together with quantization of NPs in whole cells. Even in standard set-ups sub-micron depth resolution can easily be achieved providing direct evidence on the transport of NPs into cells, as NPs at the surface of the cell can be differentiated from NPs inside the cell. This also enables a 3D map of the metal distribution in cells. These capabilities will be demonstrated using the yeast *Saccharomyces cerevisiae* as a eukaryotic cell model to study the uptake and the toxicological effects of copper oxide NPs (CuO-NPs). The Cu distribution in whole cryopreserved cells was visualised and the 3D reconstruction of the Cu distribution proved that Cu derived from CuO-NPs accumulated inside cells.

## **Dynamic metal ion speciation by voltammetric methods**

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It is well established that the total metal concentration in natural media is rarely adequate to interpret the reactivity of the metal ions in biological or environmental processes being speciation the key factor to understand their transport, bioavailability and toxicity. Moreover, because natural systems are rarely at chemical equilibrium dynamic speciation is necessary to understand the non-equilibrium properties.

Voltammetric methods due to their basic principles can give information on dynamic speciation without combination with additional separation techniques. Indeed the voltammetric signal depends not only on parameters representative of the solution thermodynamic equilibrium but also on kinetic factors such the rate of mass transfer in solution and the features of interconversion of metal complex species. Additionally most voltammetric methods are sensitive enough to be readily employable at the relevant natural media concentrations.

In this work the usefulness of voltammetry for dynamic metal ion speciation will be discussed. Several examples will be presented oriented to copper, lead, cadmium, zinc, and nickel due to the biological and environmental relevance of these elements.

## **HEAVY METALS IN SEAFOOD IN A CHANGING ENVIRONMENT: SPECIATION, DETECTION, EFFECTS, IMPACTS IN PUBLIC HEALTH AND MITIGATION STRATEGIES**

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### **Introduction**

Seafood is recognised as a high-quality, healthy and safe food and is one of the most important commodities consumed worldwide. However, seafood, like other types of food, can also be a source of harmful environmental contaminants with potential to impact on human health, including heavy metals. Availability of safe and high-quality food is a growing public concern and research plays a very important role in ensuring consumer confidence in this sector. Therefore, there is an urgent need to assess food safety issues related to contaminants, including those of emerging concern like heavy metal speciation, and evaluate their impact on public health in order to increase seafood safety and reduce human health risks.

### **The ECsafeSEAFOOD project**

ECsafeSEAFOOD is a four-year EC FP7-funded project coordinated by Instituto Português do Mar e da Atmosfera (IPMA, I.P.) that brings together a multidisciplinary consortium of 17 institutions from nine EU countries and Norway. This project focuses on research in seafood safety assessment of contaminants of emerging concern present in seafood as a result of environmental contamination and on the evaluation of their impact on public health.

### **Main results**

The project has determined the prevalence of heavy metal species (including inorganic As and MeHg) of emerging concern in specific commercial seafood species from different locations around Europe, including the assessment of the effects of cooking and processing procedures on these contaminants. The effects of global warming on bioaccumulation and elimination of heavy metal species, assessment of their transfer between the environment and marine biota, and their toxicological impact on public health are also being screened. These findings are being integrated in the exposure assessment to consumers. Additionally, the assessment of the use of macroalgae to remove environmental contaminants (phycoremediation), and an online tool for interest groups are being tested as mitigation strategies to minimise potential risks for consumers.

As this vital information comes to light, it is being communicated to local food safety authorities so that they can: a) implement measures to help prevent adverse health effects due to contaminant consumption, and b) confirm/refine the European Maximum Reference Levels (MRLs) in seafood for contaminants that are real hazards and for which no legislation exists or the information is still insufficient.

The project is also developing sensitive and rapid screening methods for targeted contaminants, including MeHg and inorganic As. These detection tools are suitable for screening of large numbers of samples and are developed for uptake by environmental monitoring agencies, research and analytical laboratories.

### **Impact**

Ensuring availability of safe and high-quality seafood to European consumers through increased information on contaminant exposure and toxicological impacts is of utmost importance, as well as development of new detection tools. Improved knowledge on the presence of priority contaminants in the most consumed seafood in the EU will enable dietary advice for reduced contaminant exposure. This will enhance consumer confidence thus strengthening the competitiveness and economic effects of producers of seafood products in the EU.

### **Acknowledgements**

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## Forensic applications of X-ray fluorescence: From heavy metals analysis to crime evidence

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Elemental analysis methods, based on the emission of characteristic X-rays by the analytes when a sample is irradiated with an energetic radiation like exciting X-ray or electron beams, have since long been used widely for the determination of major, minor and trace elements in an extensive range of both solid samples in different fields. In addition to the multi-element character (typically from sodium to uranium) and wide dynamic working range, the possibility to analyse solid samples with minimal or no sample preparation is one of the major advantages of X-ray fluorescence (XRF) spectrometry. The power of X-ray fluorescence itself is generally well acknowledged—fast non-destructive elemental analysis suitable for accurate quantitative characterisation in both % and parts per million (ppm) regimes.

Different X-ray spectroscopy based tools, just as many other analytical techniques, have been used in forensic science for several decades. Classical X-ray based techniques used in forensic work are X-ray powder diffraction (XRD), X-ray fluorescence (XRF), X-ray imaging and Energy dispersion X-ray emission linked to an electron microscope (SEM-EDX). These complementary techniques are mainly used in trace analysis. X-ray fluorescence, whilst attractive for the forensic analyst, sometimes cannot be applied because in the majority of cases crime scene specimens are microscopic in nature. A conventional bench-top XRF system has an analysis spot of perhaps 2–4 cm, and is unsuited to perform, for instance, analysis of a 100 µm fragment.

During the last twenty years, noticeable development was made in the instrumental aspects of X-ray spectrometry, especially in the improvement of X-ray optics and detection systems. All this resulted in a wide variety of instrumentation becoming available today. Significant advances in focusing optics (development of collimators and polycapillary lenses) have promoted the design of micro beam XRF (µ-XRF) instrumentation employing conventional X-ray tubes as the source of primary radiation. The use of automatized XYZ stages allows the possibility to do point, line profile or mapping analyses. A microscopic particle from a crime scene can be directly analysed without any sample preparation, simply located using optical cameras, and subsequently characterized for elemental content. Furthermore XRF mapping creates detailed element distribution maps of heterogeneous materials.

In this presentation we will illustrate the use of µ-XRF in different analytical case studies of materials of forensic interest such as glass fragments, vegetation, gunshot residues, coins and banknotes.

## Heavy metal assessment in main Iberian estuaries (Douro, Tagus and Guadiana) and adjacent continental shelf

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Sediment load carried by rivers to estuaries and to the continental shelf can be highly modified by a range of diverse anthropic activities. Also, the frequency of floods as well as their magnitude progressively decreases with damming, depriving rivers of their capacity to clean their hydrographic basins of accumulated sediment.

Several important rivers, some of them having their source in Spain, with many tributaries, flow across the Portuguese territory and develop estuaries with different typologies along the Portuguese coastal area. Their drainage basins have striking differences, either natural: run-off, outcropping lithologies, climate, geomorphology, vegetation cover; and/or due to human occupation: urban centres, agricultural practises, industries, mining, dredging. Fluvial sediments, travelling throughout the Iberian Peninsula and being affected by many factors, are trapped in estuarine environments and/or exported towards the shelf. For some decades/centuries the ecosystems of these estuarine areas have been modified, due to the addition of components related with human activity, including heavy metals. Therefore, composition of sediment load carried by rivers draining to the Portuguese coast is highly variable.

In the present work, the heavy metal contamination of sediments from major estuaries (Douro, Tagus and Guadiana), coastal adjacent area and adjacent shelf are compared and discussed taking into account lithogenic features, main anthropogenic activities and geomorphological and oceanographic conditions.

## CALCULATION OF LINEWIDTHS AND FLUORESCENCE YIELDS

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The knowledge of accurate values of atomic parameters is essential in many branches of physics and technology such as spectroscopy, plasma physics, astrophysics, and materials science. Among these parameters, linewidths and fluorescence yields are of paramount importance. For example, fluorescence yields are routinely used in applications ranging from X-ray based analytical techniques, X-Ray fluorescence (XRF), particle-induced X-ray emission (PIXE) to electron probe micro-analysis. Knowledge of accurate linewidth values is essential for the analysis of atomic spectra.

Atomic parameters have been objects of intense research, both theoretically and experimentally, since the second half of the 20th century, and several reviews can be found in the literature, but despite the increasing number of theoretical and experimental works available concerning the determination of linewidths and fluorescence yields, available data are still scarce or outdated.

We review here recent work concerning the theoretical the determination of these parameters, for the inner shells of several elements using the multi-configuration Dirac-Fock (MCDF) method.



## Integrated Pollution Assessment for Heavy Metals in Lisbon

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The environmental contaminating metals, such as lead, cadmium, nickel and chromium present a public health problem taking into account the way they interact with the human organism. These metals are considered to be toxic since, in general, they do not take part in the living organisms' metabolic processes, which may result in their bioaccumulation. Therefore it is mandatory to monitor and quantify the presence of such metals in several ecosystems, in particular the urban environment.

The main goal of this work relied on the integrated study of urban pollution by lead, chromium, cadmium and nickel in the city of Lisbon.

The monitorization of the studied metals was performed by using environmental matrices such as poplar leaves (*Populus*), soil, air, rain water and road dust.

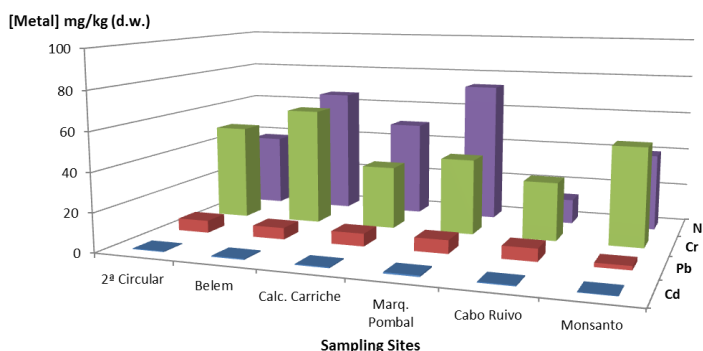
Several sites of the city were chosen for the present study, taking into consideration the local topology, housing profiles and traffic intensity.

During the studied period, from 2003 to 2011, soil and poplar leaves were sampled every year, between October and November. Road dust and atmospheric particulate matter samples were collected in 2008, between June and July, and in 2009, between January and February, while rain water was sampled in October of 2011.

The determination of the studied metals content in all samples was performed by Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The operating conditions of the spectrometer as well as the graphite furnace were optimized for each metal.

The obtained results allowed one to conclude that Calçada de Carriche, Marquês de Pombal and 2<sup>a</sup> Circular are the most polluted sites in Lisbon, mainly due to high traffic volume. On the other hand, Marquês de Pombal and Calçada de Carriche have a local valley shape topology, thus creating additional limitations to pollutants dispersion, which may have significantly influenced the obtained results [1].

Average values of soil metals contents for the six sampled sites in Lisbon are shown in the following figure.



[1] Silva, H.F.F.A. (2015), Avaliação integrada da poluição por metais tóxicos na cidade de Lisboa. PhD, FCUL, Lisboa.

**New capabilities of PIXE using microcalorimeter  
energy dispersive 10 to 20 eV resolution spectrometers**

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**Abstract:** High resolution PIXE has been for long limited to wavelength dispersive spectrometers and, although a significant amount of knowledge was gathered, applications and a few specific fundamental problems remained essentially absent from high resolution PIXE work. A first set of results on low energy PIXE obtained at the beginning of this century and the installation of the first high resolution EDS PIXE system at the end of the first decade, based on a commercial X-ray Microcalorimeter Spectrometer (XMS), opened up a horizon of new capacities for PIXE and provided new tools for fundamental atomic physics research. In this work, a short review of recently established results and evidence for these new capacities of PIXE is made, including its use in conjunction with heavy ions PIXE (HI-PIXE).

## Heavy metals: from farm to fork?

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Farming within cities is regarded as an important factor in urban development in the current century. However, many urban and suburban soils are known to have been accumulating a wide range of contaminants, particularly heavy metals, and can thus present a serious hazard if they are used for production of edible crops. Nowadays, roughly half of the world population lives in cities, and the tendency is to increase, so it is expected that the trend of urban farming will also increase.

Sometimes the allotments used for these crops are old or abandoned fields where industries used to exist, and thus the soils can be heavily contaminated, both with organic pollutants and heavy metals. The main sources of soil contamination are the result of anthropogenic activity that generates heavy metals like mines, fertilizers, industry and urban traffic. Metals like Ni, Zn, Pb, Al, Cd and Hg can remain in the soils for a long time and their removal is always difficult and expensive. Therefore, plant uptake of these contaminants can cause acute and chronic toxicity in the population even after the pollution source has been removed. Also, heavy metals like Cu, Mn and Zn are essential to plants but in excess they become toxic affecting the normal development of crops, although the accumulation of these metals is not so dangerous as they represent a lower risk for public health.

Urban farming activities in contaminated soils has been gaining increasing attention as a problem that needs to be addressed so that appropriate preventive or corrective measures can be taken, to avoid health hazards associated to the ingestion of the toxic elements via the food chain. In this work we will present an overview of the contamination risk by heavy metals in urban gardens, its effect in the growing of edible vegetables and the potential hazard to the food chain.

## Developments on large area XRF imaging system based on gaseous detector

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### Abstract:

During last decades several developments in the field of X-ray detector technology and optics associated with X-ray fluorescence techniques allowed evolving the technique from elemental analysis into space-resolved elemental imaging analysis. The knowledge of the accurate elemental composition of samples is of paramount importance in studies regarding toxic element contamination, dating of artworks, migration of elements from amalgam to tooth. However, this knowledge is often not enough and information regarding the distribution of the elements in the samples is fundamental to the understanding of basic mechanisms.

When large areas of detection with position and energy resolution are needed in the radiation detection field, micropatterned gaseous detectors (MPGDs) can be an interesting and unique solution in some cases.

The 'holy grail' of EDXRF elemental imaging is acquiring elemental images of areas larger than the probe beam spot size. The use of a large area elemental imaging MPGD is an elegant approach for a long standing problem. Former works [1], [2] and [3] have already shown good prospects and promising results in the field. These systems have high detection efficiency (e.g, 95% at 5.9 keV and 25% for 17.5 keV), energy resolution of 18% at 5.9 keV and are capable of producing images of energy dispersive X-ray fluorescence with a resolution below 300  $\mu\text{m}$  for applications in many science and life-science fields.

X-ray fluorescence imaging (XRFI) analysis of different samples using systems based on MPGDs will be presented.

[1] A. L. M. Silva et al., Performance of a gaseous detector based energy dispersive X-ray fluorescence imaging system: Analysis of human teeth treated with dental amalgam", *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2013.

[2] A Zielinska, W Dabrowski, T Fiutowski, B Mindur, P Wiacek and P Wrobel, X-ray fluorescence imaging system for fast mapping of pigment distributions in cultural heritage paintings JINST 8 P10011 2013

[3] A. L. M. Silva, M. L. Carvalho, K. Janssens and J. F. C. A. Veloso, A large area full-field EDXRF imaging system based on a THCOBRA gaseous detector" *JAAS*, 30, 343 - 352, 2015 DOI: 10.1039/c4ja00301b (2015)

## The Gas Proportional Scintillation Counter for X-Ray Spectrometry

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**Abstract:** Gaseous radiation detectors are very good detectors for x-ray spectrometry. However, while common solid-state x-ray detectors present energy resolutions around 150 eV, for 6 keV, the commonly used proportional (ionisation) counter may reach energy resolutions of only ~800 eV. In addition, modern gaseous detectors based on hole-type structures for signal (charge) amplification may present even worse energy resolutions. Nevertheless, gaseous detectors present advantages over the solid-state ones, such as room temperature operation and large detection areas with low-cost 2D-imaging capabilities.

Gas Proportional Scintillation Counters (GPSC) are gaseous x-ray detectors where the charge signal produced by the x-ray interaction is amplified through gas secondary scintillation processes, in opposition to the charge avalanche amplification processes commonly used in gaseous detectors applied to x-ray spectrometry.

In gaseous detectors, the electrons produced in the x-ray interaction with the gas medium are driven towards a region where the electric field is large enough to promote signal amplification. For GPSCs, the applied electric field is only high enough to excite but not ionise the noble gas atoms, producing a scintillation-pulse, in the atom's de-excitation, which is proportional to the number of electrons produced in the x-ray interaction. As the statistical fluctuations inherent to the scintillation process are much less than those associated to the avalanche ionisation processes and even less than those associated to the charge produced by the x-ray interactions, GPSCs may reach energy resolutions around 450 eV, for 6 keV x-rays. On the other hand, they need a much cleaner noble gas and higher voltages applied for optimal operation.

The application of GPSCs to EDXRF has been very limited, mostly due to the use of photomultiplier tubes (PMT) for the scintillation readout. These photosensors are fragile, bulky and power consuming devices. The solid-state large area avalanche photodiodes, developed in the last two decades, did not present a significant alternative to PMTs due to their limited sensitive area and to their high-cost/sensitive-area when compared to PMTs. On the other hand, the recent development of silicon-photomultipliers, SiPMs, may allow to build a large-area, yet compact, low power-consuming and cost-effective photosensor readout with 2D-imaging capabilities.

It is possible, thus, to have a competitive GPSC for X-Ray Spectrometry applications, where a large detection area is an important asset.

In this talk, we will review the GPSCs, their operation principles and performance, and present some examples of their EDXRF capabilities.

## Toxic Metals in Tattoo Ink

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Tattooing practice is adopted worldwide and represents a socio-cultural phenomenon, but the injection into the skin of coloring agents, such as metals might pose a serious health problem. Tattoo ink compounds are in general not officially controlled. Moreover, the origins as well as the chemical and toxicological specifications of these coloring agents are hardly known by the producers, the tattooists and by the consumers [1]. In this view, the aim of this study was to characterize the metal composition of tattoo inks available in the market and to draw attention to the associated risk for human health.

A set of tattoo inks from the brand Kuro Sumi® was analyzed by means of Synchrotron-based X-ray Fluorescence spectrometry (Sy-XRF) at BAMline @ BESSY II and Raman Spectroscopy using the XploRA confocal Raman microscope (785 nm laser). Carbon black, rutile, phtalo blue, phtalo green, helizarin red, helizarin yellow and dioxazine violet were respectively identified in black, white, blue, green, red, yellow and violet inks. However, a wide range of transition and heavy metals, potentially hazardous was revealed by Sy-XRF. A semi-quantitative evaluation has revealed, in some inks, amounts of Cr, Cu, Zn and Pb higher than the allowed according to the resolution adopted by the Council of Europe on the safety of tattoos and permanent make-up (PMU) [2].

[1] C. de Cuyper (2010) Materials Used in Body Art, in Dermatologic Complications with Body Art - Tattoos, Piercing and Permanent Make-Up, M.L. Cotapos and C. de Cuyper, Editors, Springer-Verlag Berlin Heidelberg.

[2] C. of Europe (2008) Resolution ResAP(2008)1 on requirements and criteria for the safety of tattoos and permanent make-up (superseding Resolution ResAP(2003)2 on tattoos and permanent make-up).

## Heavy metals on the skin: Assessment of heavy-metals in cosmetic-products

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The use of cosmetic products in the last decades has been increasing in the world. Until the decade of 1980 the major producers were located in Europe and in the United States. Nowadays the producers of India, China, Brazil and other emergent economies are important players in this market that had the estimated global value of 460 billion U.S. dollars in 2014. The market share is dominated (35%) by the countries of the Asia-Pacific Region followed by Western Europe and North America [1].

Usually cosmetics are repeatedly applied directly on the human skin, mucous membranes, nails and hair, direct ways of absorption by the human body. These products should be safe for health but recently there has been increasing concern about their safety. Several studies have detected substances with adverse effects, namely natural and chemical substances including heavy metals. Lead, mercury, cadmium, chromium, arsenic and nickel, as well as aluminium, classified as a light metal, are detected in various types of cosmetics, body care products and hair cosmetics. These metals may undergo retention and act directly on the skin, be absorbed through the skin into the blood or accumulate in the body and cause toxic effects in various organs. This situation is also a major concern in the European Union due the opening of the European market to the world. Under European legislation, all cosmetics, permitted for use, should be completely safe for users and the final responsibility for ensuring the safety of these products lies with the manufacturers, distributors and importers [2]. However the observed effective capacity of health safety guarantee for these products has many limitations considering the enormous number of brands, origin and products for sale.

To evaluate health safety in terms of toxic heavy metals, the content of lead, chromium, cadmium and nickel was evaluated in 34 samples of cosmetics on sale in Portugal. The metals content of the samples has been determinate by graphite furnace atomic absorption spectroscopy (GFAAS) after reduction to ashes an acid dissolution. The resume of the results are shown in the following table.

Percentage of samples where the Metals are detected				
Cosmetic type	Pb	Cd	Cr	Ni
Lipstick	33%	33%	100%	67%
Lipploss	38%	0%	38%	0%
Face Powders	100%	100%	100%	100%
Deodorant	0%	0%	50%	0%
Under-Eye Concealer	40%	0%	80%	60%

We have confirmed the presence of toxic metal in these products and in amounts capable of creating danger to human health. Considering the growing usage of cosmetics, nowadays also in the young population, it is necessary to pay special attention to these problems and design a better control framework, capable of guarantee effectively the safety for users of the cosmetics on sale.

[1] Cosmetics Europe - The Personal Care Association, 2014 Annual Report.

[2] Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products, Official Journal of the European Union.

### **Determination of high amounts of mercury in human samples: the use of mercury in medicine**

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Since ancient times the history of mercury has been connected with that of medicine. The use of mercury in medicine repeatedly led to controversies because of toxic effects which often were very difficult to differentiate from the symptoms of the disease for which the metal was administered. Moreover, the use of mercury-based amalgam fillings is still common practice in dentistry nowadays, especially regarding children.

In this work we report the determination of high amounts of mercury in human samples using Energy Dispersive X Ray spectrometry (EDXRF). Quantitative evaluation was carried out using the Fundamental Parameters method. Two case studies were selected to illustrate these applications. The first one relates with the analysis of human remains from an individual buried in the 18<sup>th</sup> century in a church in Almada. Samples of hair and bones were analyzed and the amount of Hg in hair arose to 5%. In the second case study, 10 human teeth treated with dental amalgam were analyzed to investigate the diffusion of its constituents. The used EDXRF setup, features a polycapillary lens to focus radiation up to 25  $\mu\text{m}$  allowing the mapping of the elemental distribution in the samples. Mercury concentration profiles showed strong levels of this element close to the amalgam region, decreasing significantly in the dentin, and increasing again up to 40000  $\mu\text{g/g}$  in the cavity where the pulp used to exist when the tooth was vital.



## Muzzle to target distance determination by X-ray fluorescence spectrometry

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In criminal investigation, one of the most important aspects of a shooting incident is the target-to-muzzle distance determination. This determination can establish the relative positions of the shooter and the victim or even help to establish the shooter's intent.

Forensic laboratories use chemographic tests as the standard procedure for this kind of analysis. These tests require the preparation of several chemical reactions and imply the partial destruction of the tested samples.

In this work we used micro-Energy Dispersive X-Ray Fluorescence ( $\mu$ -XRF), to obtain the elemental distribution of Pb, Sb, Ba, Zn and Cu in plain white cotton tissue as target material, Glock 17, 19, 26 and FN Browning High Power MKIIS handguns. Several samples were prepared by shooting pieces of cloth at several distances. Lead was found to be the element present in higher concentration, reaching 1000  $\mu$ g/g in some cases, followed by Sb, Ba, Zn and Cu. Four squares (4x3 cm<sup>2</sup>) of each target were cut and analysed directly by  $\mu$ -XRF to obtain the elemental distributions for Cu, Zn, Sb, Ba and Pb as a function of the shoot distance.

## Silver containing electrospun wound dressings

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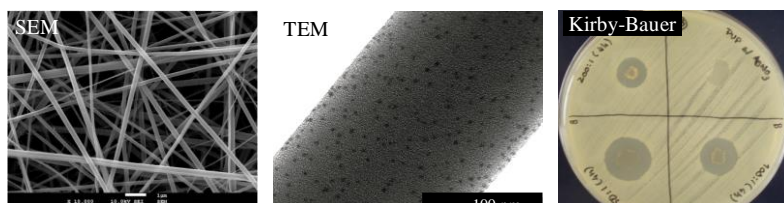
Wound dressings fabricated from electrospun fiber mats (EFMs) provide a first physical barrier to microorganisms' invasion through the wound due to their small pore size. This protection can be reinforced by the incorporation of Ag. While effective in the protection against infection, the wound dressing must be nontoxic and should not delay tissue regeneration. Cytotoxicity is a major concern regarding the incorporation of Ag in wound dressings for chronic wounds (ulcers) or extensive burns.

Ag nanoparticles (AgNPs) offer enhanced antimicrobial activity and reduced toxicity when compared to other sources of Ag. Their synthesis in a solution containing AgNO<sub>3</sub> can be achieved by nucleation of reduced Ag<sup>+</sup> in the presence of reducing and stabilizing agents. Exposure to UV light enhances AgNP formation. Some polymers promote AgNP formation and stabilization. While nanofibers incorporating AgNPs can be obtained by electrospinning a colloidal polymeric solution with AgNPs, it is also possible to achieve AgNP formation by irradiating nanofibres electrospun from solutions containing AgNO<sub>3</sub>.

We produced polyvinylpyrrolidone (PVP) EFMs from solutions containing AgNO<sub>3</sub>. EFMs' morphology was characterized by SEM. UV irradiation photocrosslinked the polymer and induced the formation of AgNPs. Both processes, as well as the release of NPs from EMs to water, were analyzed by UV-Vis spectrophotometry. Weight loss of EMs when immersed in water was measured to evaluate photocrosslinking efficiency. NPs were characterized by TEM. Their activity against several microorganisms was assessed by disk diffusion/minimal inhibitory concentration. Cytotoxic effects were evaluated by in vitro cell viability tests, incubating epithelial cells (Vero cell line) in medium that had been previously conditioned by the mats.

Results indicate that as UV irradiation time increases the EMs weight loss decreases and absorbance at 290 nm (due to photocrosslinked PVP) increases. When either the ratio of AgNO<sub>3</sub>:PVP used or the UV irradiation time increases, the mean NPs size (all below 10 nm) and the dispersion of particles size increase. The AgNPs originate an absorbance peak (around 425 nm) which increases during the first 4h of irradiation, then stabilizes, and shifts as the NPs mean size in a sample increases. The concentration of NPs released to water from an immersed EFM increases in the first 2h. All EFMs showed inhibitory effects on the microorganisms tested. Cytotoxic effects were not found below the concentration of 3,2 µg/ml for the ratio (content of Ag in the mat) / (ml of conditioned medium) while medium conditioned by AgNO<sub>3</sub> exhibited toxicity when the Ag content is greater than 1,5 µg/ml.

Electrospun fiber mats containing AgNPs are an effective wound dressing regarding the protection of the wound from invading microorganisms while avoiding cytotoxic effects caused by high Ag concentrations.



## Deteção de elementos traço radioativos por espectrometria alfa

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Os radionuclídeos naturais podem ser utilizados como rastreadores de diversos fenómenos da natureza, nomeadamente alterações climáticas, ou então como elementos de datação de rochas ou de artefactos metálicos [1]. Neste trabalho é apresentada a metodologia empregue na quantificação de elementos traço radioativos por espectrometria alfa e os resultados obtidos para: - uma amostra de sedimentos de corrente, depois de homogeneizada e regularizada, colhida numa área que apresenta uma anomalia geoquímica natural de urânio; - materiais obtidos de experiências recentes de redução de metais, simulando técnicas antigas e tradicionais: (1) redução de minério de estanho com meios simples e tradicionais; (2) co-redução de minérios de estanho e de cobre reproduzindo possíveis técnicas proto-históricas.

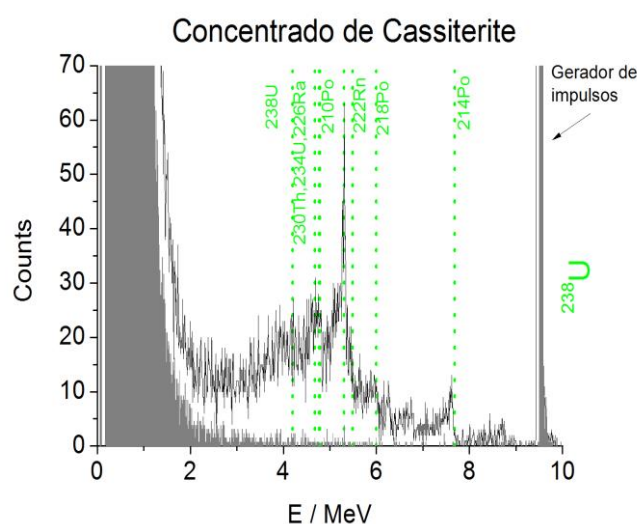


Figura 1: Espectro de emissão alfa do concentrado de cassiterite. As linhas a verde indicam as energias das partículas alfa emitidas na série radioactiva natural do <sup>238</sup>U. A cinzento surge, as contagens de fundo.

[1] I. Liritzis (2006), The dating of ancient metals: review and a possible application of the 226Ra/230Th method (a tutorial), Mediterranean Archaeology and Archaeometry, Vol.6, No 2, 2006, 81-95.

## Study of mineral translocation and accumulation in biofortified durum wheat (*Triticum durum*) and bread wheat (*Triticum aestivum*) grains

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Even in the XXI century, there are still a large group of the world population that suffers from micronutrient undernourishment, which constitutes a worldwide public health problem. These nutrition deficiencies not only are resultant from famine but also from the low nutritional value of food. Thus emerges the need of staple crops being biofortified with micronutrients such as iron (Fe) and zinc (Zn) [1]. Biofortification has the purpose of increasing these micronutrients concentration on staple food without compromising their productivity.

The aim of this study is to quantify the major and trace elements present in the physiological structures of wheat grains, to which were added, during their development, iron and zinc supplements.

The use of a  $\mu$ -XRF technique, allowed us to map and quantify the metals in the grain, allowing some insight into the metabolic elasticity, mineral translocation and accumulation on the plant.

Through the element distribution maps obtained, it was possible to verify that the micronutrients used in the wheat grains biofortification are predominantly present in the bran and embryo albeit. Fe, Mn, Zn and Ca are essentially deposited in the ventral part of the grain in the crease tissue and vascular bundle, while K is spread throughout the outer pericarp. P, on the other hand, is deposited essentially in the aleurone inner layer surrounding the endosperm and embryo.

[1] F.C Lidon et al. (2015) Crop and Pasture Science 66, CP14270

## Mine waste materials to mineral by-products from wastes: A way to increase environmental and economic value

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The study conducted in the S. Domingos, Aljustrel and Neves Corvo mines is part of research project PROMINE (Nano-particle products from new mineral resources in Europe), financed by the EU's 7th Framework Programme. Geochemical sampling campaigns were conducted to characterize the mine's wastes. The results of the study show that S. Domingos, Aljustrel and Neves Corvo mine wastes of specific piles have high concentrations of chemical elements that may be suitable for secondary exploration. Milled pyrite dump in the Achada do Gamo area (S. Domingos) contain high concentrations of Sb and Ge up to 30 times the Crust abundance (1.5 mg kg<sup>-1</sup>) as well as Re, Zn and Fe [1]. Rhenium concentrations above 3 mg kg<sup>-1</sup> were found and therefore subsequently studied in those waste piles [2]. Most probably the very high concentrations of rhenium are not due to its concentrations in the primary ore, but in the ash deposits lining the chimneys of the sulphur plants at Achada do Gamo. Rhenium's high capacity to volatilize during pyrite burning also probably justifies the high concentrations found in the waste materials nearby the chimneys. Nevertheless, it's high return in economic world markets justified spectroscopic studies using synchrotron radiation in the ESRF facilities that showed the affinities of rhenium to oxygen in the analysed debris [2,3]. Other interesting concentrations were obtained for Sn where all the concentrations obtained in a sampling profile made in that pile were above 200 mg kg<sup>-1</sup>. In the Algaes sector (Aljustrel), similar material (milled pyrite) as that found in Achada do Gamo, containing lower concentrations of those elements. This difference lies in the fact that no pyrite burning took place in Algaes and hence, no ashes were deposited in this sector [1]. However, in places such as Barreiro where the ore was transported for use in sulphur production, elevated concentrations of these elements could be found. In the Neves Corvo mine tailings pond of Cerro do Lobo, interesting concentrations for Sn, Cu, Zn, In, Co and Sb, among others, were found. These interesting materials are being researched for possible economic viability. Volumes and extractability studies were also undertaken to evaluate if those elements with economical interest can easily be separated from the mineral matrix. The economic viability of these materials will decrease the onus of future remediation costs as most of these are considered pollutants if left abandoned in mine dumps.

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[2] Figueiredo, M.O., Silva, T.P., Veiga, J.P., de Oliveira, D. & Batista, M.J. (2014). Towards the recovery of by-product metals from mine wastes: an X-ray absorption spectroscopy study on the binding state of rhenium in debris from a centennial Iberian Pyrite Belt mine. *Journal of Minerals and Materials Characterization and Engineering*, **2**, 135-143.

[3] Silva, T.P., Veiga, J.P., de Oliveira, D., Batista, M.J., Rosa, D. & Figueiredo, M.O., 2015. A utilização da radiação de sincrotrão no estudo de materiais geológicos: Breve abordagem sobre experiências recentes de um grupo de utilizadores. *Geonovas*, **28**, 111-119.

## Trace element contamination and availability in Fildes Peninsula, King George Island, Antarctica'

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Although Antarctica is often considered a remote and pristine environment, some ice-free areas have been subject to human impacts for 50 years or more. The Ardley Cove area (located on Maxwell Bay shoreline, Fildes Peninsula, King George Island, Antarctica) is characterized by its high biodiversity, but also by a high density of scientific stations, making it potentially one of the most impacted areas of Antarctica. In order to assess the source, contamination level, distribution and availability of several trace elements (Cr, Ni, Cu, Zn, As, Pb, Cd and Hg) soil samples were collected around Maxwell Bay. Soils were also collected in the study reference site near the Bellingshausen Dome area, as it lies far from center of human activity and associated infrastructure. The results obtained in this study pointed to the existence of several contamination hotspots, mainly related to high levels of Zn, Pb, Cd, Cr and Ni. Enrichment factors (EFs) and sequential extractions were also used to assess the degree of contamination and availability of the trace elements under investigation. In particular, higher extraction proportions were obtained for Zn and Pb (68 and 71%, respectively), which were also the same elements where the highest EFs were determined. The results obtained in this study clearly point to human impact on the natural environment in this region of Antarctica and we recommend the implementation of appropriate contamination control and remediation methodologies.

### Acknowledgements

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### **Risk-Benefit assessment of raw and cooked farmed gilthead seabream consumption taking into account the bioaccessibility data**

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The composition of raw and cooked gilthead seabream (*Sparus aurata*) was analysed with particular emphasis on Se and some contaminants. The bioaccessibility of Se, As, Hg, and MeHg in raw and cooked gilthead seabream was also studied by using an *in vitro* digestion method. Moreover, a risk-benefit assessment of different seabream consumption scenarios was performed on the basis of data obtained before and after the *in vitro* simulation of the digestion process (bioaccessibility). It was found that grilling and roasting caused the most significant changes in the composition of gilthead seabream. Particularly, the contaminants Hg and As displayed a significant increase with every culinary treatment, only As in boiled gilthead seabream did not increase. Regarding bioaccessibility, while the share of As rendered bioaccessible after digestion was always very high (over 96 %), the share of Hg (and MeHg) available for intestinal absorption was reduced by cooking, especially by grilling, 39 % (60 %) and roasting, 38 % (55 %). The risk-benefit probabilistic assessment leads to an advice of not exceeding one weekly meal of gilthead seabream consumption. This recommendation concerns mainly pregnant and nursing women. On the other hand, Se bioaccessibility was high — minimum of 85 % in boiled seabream—, thus helping to balance the deleterious effects of MeHg. This was corroborated by the Se:Hg molar ratios and Se Health Benefit Values. Hence, the MeHg risk in grilled and roasted seabream seems to be low.

**Keywords:** gilthead seabream, essential and contaminants elements, bioaccessibility, risk-benefit assessment

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## Arsenic determination in two different species of eucalyptus growing in artificial contaminated soils – portable X-ray fluorescence *versus* triaxial-XRF technique

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Phytoremediation is an economically feasible technique used for reclamation of contaminated soils with toxic heavy metals. In order to evaluate the uptake capabilities of two different species of eucalyptus (*Eucalyptus globulus* Labill. and *Eucalyptus nitens* Maiden) growing in artificial contaminated soils with 100  $\mu\text{g g}^{-1}$  and 200  $\mu\text{g g}^{-1}$  As, a study was conducted during 6 months. Roots and leaf samples were collected every 2 months, and As was measured using both a portable X-ray fluorescence system and a triaxial-XRF technique. The results of these techniques were compared in terms of accuracy and effectiveness. Arsenic was not detected in control plants of both species, but accumulates in the roots until the 4<sup>th</sup> month, decreasing afterwards. On average, the higher As concentrations were always noted in the roots of *E. nitens* with values >100  $\mu\text{g g}^{-1}$  As in plants treated with 200  $\mu\text{g g}^{-1}$  As. The evolution of As accumulation in roots of *E. globulus* throughout the experiment is shown in figure 1. Arsenic was not detected in *E. globulus* leaves during the first 4 months, although in *E. nitens* leaves this toxic element has been detected after 2 months of treatment with the highest As concentration (200  $\mu\text{g g}^{-1}$  As), reaching values > 10  $\mu\text{g g}^{-1}$  As, which were fairly maintained throughout the experiment.

Globally, the As values obtained by both methods are in agreement, although in the leaves, triaxial-XRF technique outperforms the portable X-ray fluorescence spectrometer due to the fact that the values are very close to the detection limits.

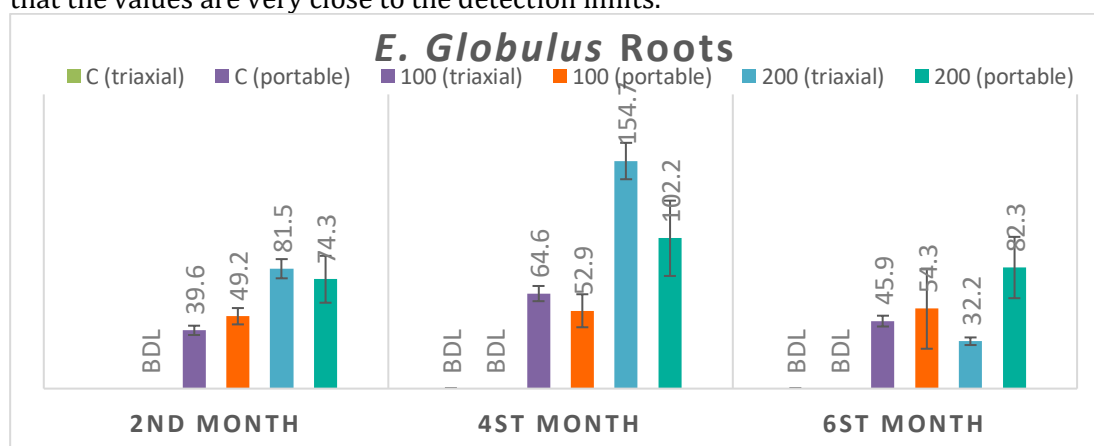


Fig 1. – Evolution of As accumulation in roots of *E. globulus* throughout the experiment. Values are expressed in  $\mu\text{g g}^{-1}$  on a dry weight basis. BDL=below detection limit; each bar represents the mean  $\pm$ SD (n =3).



## Synchrotron radiation and Nanophysics

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Applications of High Resolution Photoelectron Spectroscopy induced by Synchrotron Radiation, in the study and analysis *in-situ* of nano-structures growth on ultra-thin films of semiconductors oxide will be presented and discussed [1].

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## Catechins: natural antioxidants against oxidative deterioration of DNA

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The reactive oxygen species coming from normal metabolic processes inside body or from exposure to heavy metals and ultra-violet radiation, trigger tremendous deleterious effects on biomolecules such as DNA and RNA. The design of new formulations of antioxidants delivery systems is essential to disseminate the lipid and biomolecules oxidation induced by oxidative stress. Catechins are tea-dietary antioxidants<sup>[1]</sup> which strongly act as metal-chelator and scavenger of the reactive species in order to decrease the oxidative stress rate. These molecules also prevent the cancer progression through the modulation of some genes and enzymes involved in cellular processes such as apoptosis, cell cycle, angiogenesis and metastasis.<sup>[2,3,4]</sup> Therefore, our research interests are centered in design stable liposomes carrying large amount of catechins to be delivered into cells. During this work, aqueous solutions of liposomes were irradiated with UV germicidal light in the presence of catechins for different time exposures. Our preliminary results suggest that catechins act as reactive species scavengers in order to decrease the liposomes oxidation induced by UV light.

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## The potential of Micro-AMS for environmental actinide studies

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**Abstract:** The Micro-AMS (micro-beam Accelerator Mass Spectrometry) system present at LATR-CTN is the former AUSTRALIS system developed by Sie et al. [1] at CSIRO. It was developed with the goal of using the capabilities of a SIMS system (spatial and in-depth analysis of bulk samples) connected to an AMS system that provides the possibility of resolving isobaric and molecular interferences, that in many cases spoil the detection limits of SIMS analysis.

The LPR (Laboratório de Proteção Radiológica) at CTN-IST has, as one of its missions, the analysis of environmental samples, especially in terms of the presence of radioactive contaminations. Alpha emitters are a particular concern due to their biological toxicity and long half lives. Some, like U, Th and Pa are naturally occurring, and others, like Pu and Am are anthropogenic. The measurement of such elements is usually performed by alpha spectrometry [2], which requires complex chemical separation procedures prior to time-consuming measurement times (several days). Besides the alpha emitters, <sup>241</sup>Am is measured by gamma spectrometry when its concentration in the sample is sufficiently high (which is rare), and <sup>241</sup>Pu, which is a pure beta emitter, is measured by liquid scintillation. The size of the samples necessary for analysis by alpha spectrometry is a limitation to this technique in many cases, especially when there isn't much sample material available, like, for example, in some biological sample material.

The use of AMS and SIMS in actinide environmental studies is well documented [3,4] and its applications have been growing in the last years. However, it is the first time, to our knowledge, that Micro-AMS is to be applied to the measurement of actinides in environmental studies. The technique permits the detection of the mentioned isotopes, in many cases with little or no sample preparation, and a significant less amount of sample material, and in much less time (less than 10 minutes average measurement time per sample versus several days in alpha spectrometry), due to its high sensitivity. The micro-beam can analyze micro particles directly, and establish actinide isotopic ratios (in this project the focus will be on U, Th and Pu), providing to the LPR the capability to perform forensic work such as, for instance, determination of the provenance of nuclear contamination [5] (distant source aerosols, nuclear vessels contaminated discharges in national waters). Besides this, Micro-AMS can be very powerful in terms of the analysis of uranium residues aerosols or industrial residue aerosols.

In cases where isotope concentrations are too low for Micro-AMS, the conventional AMS system at CTN-IST can be used. The extreme sensitivities of this system permits, besides the previously mentioned applications, the quantification of natural <sup>236</sup>U in the uranium mines region in the north of Portugal which cannot be measured by any other technique due to its extremely low natural abundances, therefore adding to the ongoing national radioactivity monitoring program for the regions of uranium mines and uranium legacy sites in Portugal [6].

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**Bioaccessibility of some contaminant elements from edible seaweed *Fucus spiralis***

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**Abstract:**

Edible seaweeds are known as a good source vitamins, protein and essential elements, like iodine. However, seaweed can also be a source of chemical contaminants, particularly mercury (Hg), lead (Pb) and arsenic (As). With the increased interest in seaweed consumption and in the worldwide pressure on ocean, some concerns stand out especially in terms of contaminant metals in foodstuffs for human consumption. The main objective of this work was carry out studies on the assessment of hazards associated to the consumption of edible seaweeds, taking into consideration the bioaccessibility of each compound under concern. Having that in mind, a brown seaweed, *Fucus spiralis*, from the Portuguese coast was collected and the concentrations of Hg, Cd, As and Pb were evaluated. Moreover, the bioaccessibility of the target studied elements was also evaluated by using an *in vitro* digestion method. Concerning the obtained results, it seems that Hg has a low bioaccessibility didn't appear to be bioaccessible. On the other hand, As bioaccessibility was around 60% whereas Cd and Pb reached to 84% and 96%, respectively. The attained results are a very meaningful contribution for a more realistic and informed assessment of the risks due to seaweed consumption, thereby being important for consumers' choices and public health stakeholders.

**Keywords:** Seaweeds, contaminants elements, bioaccessibility, hazards

### **Assembly of a portable X-Ray fluorescence spectrometer with tri-axial geometry**

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The aim of this work is to build a portable XRF setup with tri-axial geometry in between the X-ray tube, the secondary target and the sample. The extensive range of applications of portable XRF spectrometers results predominantly from their portability, multi-element capability, fast analysis times, minimal sample preparation requirements, and non-destructive nature [1].

The advantages of this tri-axial geometry relates to the decreasing effects of scattered X-rays that do not contribute to photoelectric effect, by polarization. This allows nearly only monochromatic excitation energy, leading to lower background, lower detection limits, hence greater sensitivity.

The assembled setup consists on the Oxford XTF5011 x-ray tube (max. power 50 W) with Mo anode. In order to take advantage of the K-lines of the x-ray tube, an Yttrium (Y) target was chosen to act as monochromator and polarizer. Characteristic radiation from the sample is collected using a Vortex® SDD detector.

This portable XRF spectrometer attends to the growing need to investigate artifacts of cultural value as well as forensic sciences samples with non-destructive in situ techniques, so results will be presented regarding the analysis of a 1779 paper document and bone remains belonging to an individual buried in the mid-18<sup>th</sup> to early 19<sup>th</sup> centuries.

The capabilities and drawbacks of the developed setup will be compared with a benchtop tri-axial setup and a portable setup with conventional geometry.

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## A Simulation of the NIST vacuum double crystal spectrometer

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Precise data of atomic parameters related to x-ray interactions with matter, often known as Fundamental Parameters, are needed for a broad spectrum of fields, ranging from medical applications to environmental control [1]. Some of the tabulated values in the latest comprehensive collection of x-ray transition energies [2] do not provide reliable uncertainties and there is ambiguity about the use of many of the tabulated values. This can provide limitation to x-ray based technologies primarily in the field of atomic physics.

Among many international institutes that participate in this initiative, the group dedicated to x-ray standards of the National Institute of Standards and Technology (NIST) is revitalizing a state-of-the-art vacuum double crystal spectrometer for ppm (part-per-million) measurements of energies in the x-ray regime.

In collaboration with NIST, the group LIBPhys is performing simulations of the spectrometer's performance with a custom-made ray-trace code developed for this kind of spectrometers [3]. In the present work, we performed several tests to the effect of vertical divergence and analyze possible methods for applying corrections. Furthermore, we are also in the process of working out a method to retrieve linewidths in complex spectra with the help of the simulation code.

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## Impacto dos elementos pesados na saúde óssea

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A Doença Óssea de Paget (DOP) é uma doença óssea rara que em certas condições pode comprometer severamente a qualidade de vida dos indivíduos afectados. Em Portugal, a doença é encontrada sobretudo no Alentejo. Os genes acometidos estão claramente identificados mas desconhece-se o factor que é responsável pela manifestação da doença, podendo estar relacionado com uma infecção viral das células ósseas ou com uma exposição ambiental.

Foram analisadas amostras da cabeça de um fémur afectado com DOP por micro-XRF e por PIXE para análise de elementos maioritários (razão Ca/P) e de elementos traço no osso, tendo sido detectadas elevadas concentrações de chumbo, na ordem dos 40 ppm, por comparação com o osso de controlo. O chumbo é um metal pesado de grande toxicidade para o osso, pois tem grande afinidade para a matriz substituindo o Ca que é assim libertado do osso. Esta substituição provoca defeitos na matriz óssea e além disso, o chumbo actua ao nível celular interferindo negativamente nos processos de remodelação óssea. Outro estudo publicado recentemente refere também a presença de elevadas concentrações de chumbo em osso afectado com DOP [1].

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## Heavy elements in chestnuts

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Chestnut fruit (*Castanea sativa* Miller) are an important food resource in several countries. Portugal is the third largest European producer, with an average production of 25 thousand tons [1], being mainly produced in the North region of Trás-os-Montes.

Earlier studies on chestnuts elemental composition were performed by atomic absorption to detect Ca, Mg, Na, K, Cu, Fe, Mn and Zn or by UV-VIS spectrophotometry to detect P [2-3].

In this work the elemental composition of two cultivars (Longal and Judia) of *Castanea sativa* Miller were studied by means of PIXE (Proton Induced X-ray Emission), using a broad proton beam at CTN-IST, Lisbon. Element identification (from Si to Pb) and quantification (following the method described in [4]) was done.

Preliminary results show different composition according with the cultivar, not only in the major and minor elements (as it is described in the bibliography) but also in the trace elements, which includes the presence of Pb and other heavy elements.

These preliminary results are part of a wider project that aims to evaluate chestnut fruits decontamination treatment with high energy electron beam and X-rays technology.

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## A robust large area x-ray imaging system based on 100 $\mu\text{m}$ thick Gas Electron Multiplier (GEM)

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Abstract: X-ray imaging applications with Gas Electron Multipliers as amplification devices traditionally make use of discrete channel readout. These solutions provide excellent spatial resolution (of the order of hundreds of  $\mu\text{m}$ ) for areas as large as  $10 \times 10 \text{ cm}^2$ . However they require complex and expensive electronic systems. For applications where spatial resolutions in the order of the mm are required, a simpler and cheaper solution is to determine the position of the interaction using the resistive charge division method. This solution greatly simplifies the electronic system, since it requires a minimum of only 4 readout channels to achieve 2D imaging over large areas. It is however very much dependent on obtaining a high signal-to-noise ratio. This means that the GEM's must be operated at high gain and, in some cases, near the discharge limit. The consequence of operating at such a regime is the higher probability of discharge, hence higher probability of detector damage.

We have developed a non-standard GEM, made from a 100 micron thick kapton foil (2-fold thicker than standard GEM's). The 100 micron thick GEM is produced using the same wet etching technique as the standard GEM and has already proven [1] to be virtually immune to the damage caused by discharges, creating a robust detector that can safely operate at the high gains necessary to achieve an adequate signal-to-noise ratio for imaging applications.

In this work we present the results obtained with a detector composed by two 100 micron thick GEM and a  $10 \times 10 \text{ cm}^2$  2D readout electrode with resistive lines. We have recorded energy resolution of 21% and charge gains above  $10^4$  when the detector was irradiated with 5.9 keV X-rays emitted by a  $^{55}\text{Fe}$  radioactive source. We also present some  $10 \times 10 \text{ cm}^2$  images acquired with our detector when irradiating a target with X-rays from an X-ray tube and the results of our investigations aiming to maximize the signal-to-noise ratio.

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## Development and characterization of thin films of graphene oxide organic devices by layer-by-layer technique to capture solar energy

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The development of organic thin film devices to capture and conversion of solar energy into electrical energy, based on photoactive polymer materials represent a promising technology capable of providing energy at low cost and easily available [1]. In this study, devices have been produced using different substrates, on which were deposited thin films of graphene oxide (GO) as cast and films with alternating layers of poly (allylamine hydrochloride) (PAH) and GO produced by the layer-by-layer (LbL) technique. To finalize the devices, electrodes of aluminium (Al films), were deposited or by sputtering or by thermal evaporation, above the PAH/GO LbL films and GO cast films prepared on fluorine-doped tin oxide (FTO) substrates. The characterization of the optical properties of PAH/GO LbL films and GO cast films, was performed using UV-Vis spectroscopy, vacuum ultraviolet spectroscopy (VUV) and infrared Fourier transform spectroscopy (FTIR). The UV-Vis and VUV spectroscopy measurements of PAH/GO films showed a linear increase in absorbance with the increase of the number of deposited bilayers, allowing the calculation with some precision of the thickness of each bilayer. Studies were also made on the GO and PAH/GO films using VUV spectroscopy, allowing the determination of the positions of the bands as well as their full widths at half maximum (FWHM). The adsorption kinetics studies on FTO substrates with 10 bilayers of GO and PAH prepared by LbL technique reveal typical adsorption behaviour of small molecules on LbL films. The morphological characterization of the films properties was performed through optical microscopy (OM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Through the OM images it was possible to conclude that the films are uniform and they present a few agglomerates. By AFM measurements was observed that the PAH/GO films grow in the form of columns and that GO is completely adsorbed on the PAH layer, having a mean square roughness (RMS) of 3.09 and 5.76 nm for the films of PAH/GO with two bilayers films and twenty bilayers, respectively. The electrical properties of the produced films were characterized by impedance spectroscopy and I-V measurements, showing typical semiconductor behaviour.

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## Metal Contaminants in Japanese-clam (*Ruditapes philippinarum*) from Tagus Estuary (Portugal)

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**Abstract:** Tagus River Estuary (ETJ) is the largest estuary in Portugal and has several uses, including fishing and aquaculture, in spite of being subject to industrial and urban pollution, with evidences of metal contamination and high faecal levels.

The production of bivalve molluscs in this ecosystem has increased in recent years due mainly to the introduction of exotic species with high adaptability and growth in this habitat, particularly the Japanese-clam (*Ruditapes philippinarum*). This outgrowth has contributed to the decline of the bivalve indigenous species populations. According to the European Union, levels of some chemical contaminants in bivalves from harvesting areas, for human consumption, have to be lower than legal limits, namely cadmium (Cd), lead (Pb) and mercury (Hg) [1,2]. Given the lack of information about this exotic species, the main purpose of this study was to evaluate the metal contamination of Japanese-clam (*Ruditapes philippinarum*), from ETJ, in reference and new sampling points, identifying potential hot spots. Preliminary results of Japanese-clam for Cd, Hg, and Pb revealed levels below the legal limits, respectively 1.0, 0.50 and 1.50 mg/kg, although some samples presented Pb levels close to 1.0 mg/kg in two critical areas. Concerning other metals such as copper (Cu) or zinc (Zn), contents were between 1 - 17 mg/kg and 13 - 21 mg/kg respectively, however 50 % of values are identical in those two areas. Moreover, levels of Cu showed a bigger fluctuation during the studied months than Zn concentrations. These results confirmed that some areas of ETJ are contaminated with Pb. This contamination can be attributed to old heavy industries deactivated. It should also be noted that these results are similar to those reported for other species of this production area, ETJ, such as furrow shell (*Scrobicularia plana*), which contains high levels of Pb, above the limit of 1.50 mg / kg and therefore its capture is prohibited [3].

**Acknowledgments:** The authors acknowledge to the project "AMETEJO" from PROMAR Program.

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## Analysis of Portuguese Olive Oils and Oil Mixtures with Impedance Spectroscopy

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**Abstract:** The extra virgin olive oil (EVOO) has a fundamental role as the main source of fat in the Mediterranean diet. This diet has been traditionally associated to longevity of the populations in the Mediterranean countries and is associated with a significant improvement in the health status, on reducing mortality in several chronic diseases [1]. As EVOO is considered a top quality product, the susceptibility to fraud increases and there is a need for research on options that detect anomalies on this product [2]. This work presents an Electronic Tongue (ET) based on Impedance Spectroscopy to classify EVOO and common olive oils as well to find adulteration of Olive oil with peanut and sunflower oils. This sensor is composed of interdigital gold electrodes deposited on a common glass solid supports, where, to improve the sensitivity of this device, thin layers of polyelectrolytes as poly(allylamine chloride)(PAH), poly[1-[4-(3-caboxy-4-hydroxyphenylazo)-benzenesulfonamide]-1,2 ethanediyl]sodium salt](PAZO) and Graphene Oxide (GO) were adsorbed by Layer-by-Layer (LbL) technique. The electrical capacitance and resistance of the samples were measured in the frequency range between 20 and 200 KHz, using a HAMEG Programmable LCR Bridge. The measured data was analyzed by the statistical Principal Component Analysis (PCA) procedure allowed to classify the different samples based on the original spectra. The obtained data allowed to conclude that different olive oils can be discriminated as well as samples of olive oil adulterated with peanut and sunflower oils can be distinguished. Thus, the ET can be seen as a taste sensor, able to classify and differentiate between samples that can be used as a complementary tool in the analysis of olive oil.

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### Heavy metal content of *Ficus carica* L. and *Cucurbita pepo* L. var. *cylindrica*, collected close an area of intense mining activity, in the Southern Portugal.

Abstract of the 2<sup>nd</sup> Workshop "Heavy metals: from the environment to the man" 21-22 March, FCT/UNL, PT  
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The so-called Iberian Pyrite Belt encompasses a large area located in the Southern of Portugal and Spain and contains one of the largest copper deposits in Europe. In Portugal the Neves-Corvo mine is the only one in fully activity. In order to evaluate the impact of mining activities in surrounding areas, soil samples as well as, leaves and fruits of *Ficus carica* L. and *Cucurbita pepo* L. were collected near mining facilities and approximately 5 Km away (background area). Both plant and soil samples were analyzed in terms of As, Cu, Pb and Zn contents by Atomic Absorption Spectrometry.

Results indicate that the leaves of both species accumulate large concentrations of metals, although in most cases metals can be removed by a simple washing process, indicating a strong aerial deposition in parallel with a weak binding mechanism at leaf surface. The total [As] in *F. carica* and *C. pepo* leaves reached 18.0 and 7.7  $\mu\text{g g}^{-1}$  respectively, but after washing with bi-distilled water these values were reduced to 11.7 and 5.1  $\mu\text{g g}^{-1}$ , respectively. Similar patterns were also observed for Cu and Pb, although for Zn the concentrations in the leaves remained similar, regardless of a washing process.

As and Pb were not detected in fruits which is a positive factor in terms of food safety and public health. In what regards Cu, fruit concentrations were 21.7 and 27.0  $\mu\text{g g}^{-1}$ , whereas Zn were 41.9 and 52.4  $\mu\text{g g}^{-1}$  for *C. pepo* and *F. carica*, respectively. The Cu levels are slightly above the critical concentration in plants (CCP) - 15-20  $\mu\text{g g}^{-1}$  Cu, while for Zn, fruit levels are clearly below CCP - 150-200  $\mu\text{g g}^{-1}$  (Kabata-Pendias, 2011). In this context, the mean dietary Cu intake must be taken into account, although some foodstuffs, particularly *Ficus* fruits, are not consumed on a regular basis due to its seasonality. Interestingly, the background levels in fruits were close to those observed in plants collected in the vicinity of mining facilities, which is probably related with an aerial dispersion of pollutants or the geochemical nature of the whole area. This further agrees with a Concentration Factor (CF) values close to 1.0, which is the ratio obtained from heavy metal concentrations in polluted and background sites ( $CF = C_{\text{pollut}}/C_{\text{background}}$ ).

The bioaccumulation factor (BAF) which determines the ability of a plant to uptake a metal from soils was calculated with the following equations:  $BAF_{\text{fruit}} = C_{\text{fruit}}/C_{\text{soil}}$ ,  $BAF_{\text{leaf}} = C_{\text{leaf}}/C_{\text{soil}}$ , where  $C_{\text{fruit}}$ ,  $C_{\text{leaf}}$ , and  $C_{\text{soil}}$  represent the metal concentrations in the fruits, leaves, and soil, respectively. The results for Cu  $BAF_{\text{fruit}} = 0.16$  and  $0.13$ , while  $BAF_{\text{leaf}} = 0.46$  and  $0.24$ , for *F. carica* and *C. pepo* respectively. The results for Zn  $BAF_{\text{fruit}} = 0.46$  and  $0.36$ , while  $BAF_{\text{leaf}} = 3.2$  and  $2.4$ , for *F. carica* and *C. pepo* respectively. The threshold and guideline values for metals in soils according to the Finnish standard values (MEF, 2007) are: for As (5  $\mu\text{g g}^{-1}$ ), Cu (100  $\mu\text{g g}^{-1}$ ), Pb (60  $\mu\text{g g}^{-1}$ ) and Zn (200  $\mu\text{g g}^{-1}$ ) which are far above the concentrations observed in our substrata in the case of Pb and Zn and far below in the case of As and Cu.

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**Precise determination of contaminants in pharmaceutical iron supplements  
with energy dispersive X-ray fluorescence technique**

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Monitoring of metal contaminants in drugs substances is an important task in modern pharmaceutical industry. This is patent in the latest replacements of chemical-based standards by instrument-based (ICP-MS and ICP-AES) standards, as proposed by international pharmacopoeias [1, 2, 3].

In this work, we employed energy dispersive X-ray fluorescence spectroscopy technique, in a triaxial geometry [4], for precise determination of elemental content in iron supplements and validate this method according to the latest regulations. Several samples acquired in Brazil, namely, Neutrofer fólico (iron glycinate), Anemifer (iron(II) sulfate monohydrate), Noripurum (iron(III)-hydroxide polymaltose complex), Sulferbel (iron(II) sulfate monohydrate) and Combiron Fólico (carbonyl iron), were analyzed and its elemental content quantified. All observable samples contain a lower content of iron compared to the prescription dose, with deviations up to 38%. Furthermore, with the present method we observe contamination of nickel and manganese in some samples.

The method was successfully validated against several certified reference materials of light organic matrices and follows the requirements of the latest regulations. We conclude that this method is appropriate for pharmaceutical purposes as provides a fast and accurate elemental determination, as well as circumvents the destruction of the sample associated with traditional methods. This method would give pharmacies and pharmaceutical control institutes the opportunity to improve their own quality control and consequently prescribe medication for which an accurate composition is known.

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**Study of trace Elements concentration in cancerous tissues by EDXRF**

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Cancer is the leading cause of death in developed countries and the second one in developing countries, where the incidence continues to increase each year. Annually about 8 million people die due to this disease [1]. Hence, the development of efficient treatments, that fall short nowadays, is highly necessary. Therefore we have to fully understand the biological and physiological processes intrinsic to the carcinogenesis. Trace elements may have an important role in this process [2], being responsible for healthy cellular growth mechanisms. These elements are responsible for a variety of metabolic processes, knowing, for instance, that they are components of different enzymes and catalysts of chemical interactions in living cells, among many others. At the biological level, they are also responsible for the activation or inhibition of enzymatic reactions and changes in the permeability of cell membranes. In addition, they appear in different concentrations in healthy and cancerous tissues due to biological changes induced by the disease.

In order to measure the element concentration and distribution we resort to X-ray Fluorescence Spectroscopy, a multi elemental analysis that relates X-ray Emission Spectrum to the specific element and its concentration. The spectrometer utilized was M4 Tornado, from Bruker, an instrument that allies non-destructive techniques with high lateral resolution, able to conduct a quantitative and qualitative analysis even when the concentrations are at the  $\mu\text{g/g}$  range. The main objective is to correlate the trace element concentrations variation between cancerous and normal human tissues in order to evaluate the influence of these variations in cancer development.

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**Analysis of the content of toxic elements in bivalve shellfish and the potential hazard to public health**

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Bivalve shellfish are of great importance in human diet, being a source of essential nutrients and providing high quality protein of biological origin. However, due to their preference for coastal regions, frequently polluted, and their feeding method, which involves filtering large amounts of water per day, the bivalves tend to accumulate trace elements in their exoskeleton and soft tissues [1]. Some, like heavy metals, may be considered a public hazard if present in trace concentrations above the limits established by the FAO (Food and Agriculture Organization of the United Nations). This study aims to establish a correlation between the concentrations of trace elements present in the soft tissues of the European cockle and its exoskeleton, and the potential threat to public health brought about by their consumption by the masses. Preliminary results, from the analysis of samples taken from the regions of Foz do Arelho and Ria de Aveiro, suggest an excess of selenium in the samples, twice above the limit established by the FAO [2], as well as the presence of excess nickel in the samples from the second region (thrice those of the first). Going forward, these results will be analyzed alongside those gathered from samples taken from various regions of the country.

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## Fast x-ray fluorescence determination of elements in vegetable materials

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Fast and reliable analytical methodologies are required for quality control of plants and vegetables in order to assure human health. Not only toxic metal elements that are present in such food need a constant check on a routine basis, but also nutritional value of essential elements must be known by the general population, e.g. in packages, as required by regulations of some countries [1, 2]. Moreover, in order to fully understand the influence of the essential elements present in vegetables it is often required the precise determination of their concentration.

Energy dispersive X-ray fluorescence (EDXRF) setup with triaxial geometry is a fast, simple and non-destructive method for multi-elemental analysis of element concentration in vegetable samples, with excellent limits of detection, and thus can be employed on a routine basis. In the present work, we analyzed the elemental content in several vegetables obtained in several local markets, with a few cases being certified as from biological production, i.e., without any chemical treatment. We performed a comparative analysis between essential elements considered relevant (K, Ca, Mn, Fe and Zn), in order to verify correlations between vegetables species (leek, lettuce, broccoli, spinach and cabbage) and localizations. Toxic metals concentrations were also verified (Br, As, Hg and Pb), with only Br being observed within the limits of detection.

We conclude that the most complete vegetable at a nutritional level is broccoli, having, if not the highest concentrations of few essential elements (Ca, Mn and Fe), at least the second one (Zn), with value very similar to the respective one of the lead vegetable (spinach). A noticeable exception is K, where broccoli contains the lowest concentration among all vegetables, having a value half of the respective one of the next lowest vegetable. This feature can be perceived as an advantage since many patients with kidney diseases [3, 4] and diabetes [5] have induced excess of potassium (hyperkalemia), which disrupts the normal human metabolism [4, 5]. Therefore, broccoli can provide an excellent source of essential elements, where ingestion of K is restricted by medical conditions.

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## Determinating the concentration of mercury and other trace elements in tissue of zebrafish (*Danio rerio*)

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Mercury (Hg) is a metal element that occurs naturally in the environment and is extremely toxic to public health. According to the World Health Organization mercury is one of the 10 chemicals of major public health concern [1].

As a model biological system, zebrafish has a wide range of information available, including the total genome sequence which presents significant homology to the human genome [2]. To assess the effects of mercury in animals, zebrafish (*Danio rerio*) were exposed for 7 days to several concentrations of Hg chloride. Three groups were studied, a control group (n=10), not exposed to mercury and two contaminated groups (n=20), exposed to mercury directly through the water. Zebrafish tissue samples were then analyzed by Energy Dispersive X-ray Fluorescence Technique (EDXRF) using the apparatus M4 Tornado™ Bruker which features a polycapillary X-ray lens allowing a beam size of only 25 μm. This technique allows us to have a multi elemental analysis as well as bidimensional maps of the elemental distribution within the fish organs and also allows quantification of the concentrations of each element present in the fish. Some samples were also analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) in order to compare the results and validate them. The aim of this study was to analyze and determine the target tissue/organs of zebrafish where mercury and other trace elements have been bio accumulated. This information allows us to shed light in the physiological process of mercury poisoning.

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