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Spectral Lines of Ca^{2+}, Au^{3+}, and Ag^{+} Found in Complex Matrices and Interactions of These Ions with Molecules, Cells and Mineral Surfaces

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Abstract: Energy Dispersive X-Ray Fluorescence (EDXRF) is a non-destructive analytical method used to solve problems involving nutritional, mineral, and toxic chemical elements. It is very common in the customization and commerce of jewelry. EDXRF depends on recording spectral lines from the irradiation of isotopes. After a brief review of the interactions of the ions Ca^{2+}, Zn^{2+}, P, Au^{3+}, and Ag^{+} along with the results of the current study it was revealed that the methodology, when used in a semi-quantitative approach, can successfully identify all elements present in a whalebone sample collected from Santa Catarina Island (Brazil). This article serves as an example to explain the molecular reactions of Ca^{2+} and the concentration of elements: Cl^{-}, Zn^{2+}, Br, Fe, Mn, Ca, K, S, P, and Si. It was proposed initially to evaluate spectral lines of Ca^{2+} found in the whalebone (biomarker). The model was then further expanded to explore Ca^{2+} and its relationships to the intra- and extracellular environments, where the plasma membrane Ca^{2+}-pump (PMCA) is responsible for Ca^{2+} ejection in most eukaryotic, excitable cells as, eg, in the cardiac tissue with a Na/Ca exchanger. The certified Road Dust (BCR-723, which is in prominence among the reference materials used) could be applied to samples of dust, soils, sediments, fossil fuel, ceramic, and bio-ceramic in general. With the aid of a matching matrix, it has been shown that EDXRF can function even with samples of Au^{3+} and Ag^{+}. The results with certified reference samples of Road Dust (BCR-723) and its standards serve as a basis for studies of catalyst supports, an eg aluminum oxide containing titanium, erbium, lanthanum, and other elements, and as a model of charged ions.

Keywords: Radiation of Isotopes, Energy Dispersive X-Ray Fluorescence (EDXRF), Calcium (Ca^{2+}), Silver (Ag^{+}) and Gold (Au^{3+}), Road Dust (BCR-723), Whalebone, Silica Gel Sensor, Electric and Hybrid Vehicles

1. Introduction

Energy Dispersive X-Ray Fluorescence (EDXRF) is a non-destructive analytical method used to resolve problems involving nutritional, mineral, and toxic chemical elements. It is typical chemical laboratories to forensic medicine medical or science detectives, legal matters, or police investigations to illustrate the use to solve mysteries. One major interest is in extracting information recorded in dust in or outside a scene of a crime, such as ash (for example coca), bones, urine, blood serum, teeth, hair, maternal placenta, milk, and, of course, guns. The method depends on the recording of spectral lines from the irradiation of isotopes.

The lives of these "experimental scientists" are devoted to investigating nature, death, or life, to discover the intrinsic laws that govern them. Scientific instrumentation is used for characterization with EDXRF nondestructive analysis, e.g., to the emerald (smaragdus = ray) with the possibility to detect the spectral lines or radiation of isotopes of the beryllium. The presence of beryllium also is in marine water, morganite, heliodor, goshenite, or bixbyite, and its green color is due to chromium and vanadium. EDXRF is not only a handful for the detection of toxic elements in customhouse and manufacturing of costume jewelry but also simultaneous nondestructive analysis of several toxicological metals in contact with the skin.

Experiments involving the interaction of electromagnetic radiation with matter have provided detailed knowledge of processes that occur in atoms and molecules. Coca leaves with neurochemical properties of cocaine (case of benzoylmethylecgonine organic compost, see below Figure 1A) or ash coca [1], which is frequently contaminated by metallic impurities e.g. iron and cadmium present in the dust in the preparation room [2, 3].

Worth noting, the medical and social issues related to its use must not be forgotten. The cognitive sequelae of cocaine abuse may be the tip of an iceberg, in particular, the violence associated with crack surpasses that of other illegal drugs and makes cocaine a societal nightmare.

When the samples are in the laboratory, the first point to be considered in the systems is the interpretation like a compartment (liquid, solid, sediments, air, etc.), and the second point is the consideration of pH-buffer solutions into systems like blood (see the Figure 1B: Channel of the transport of ions into the human circulatory system, and the focus is the plasma). So, to analyze the compartment it could be the blood (a very useful situation in cases of Pb or metallic Hg), or only plasma.

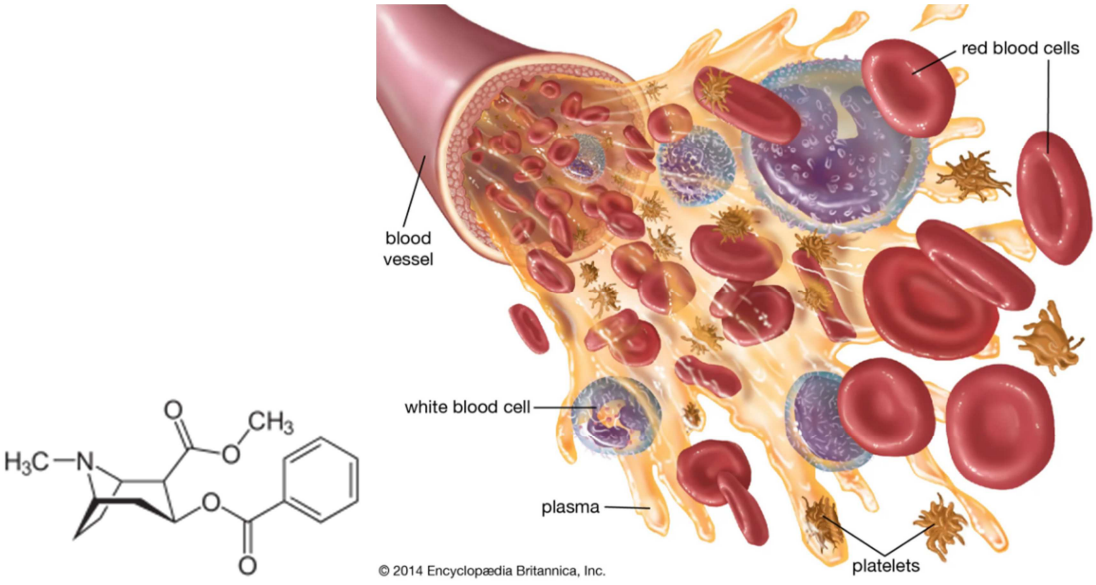


Figure 1. *A) Benzoilmetilecgonina (coca). B) Channel of the transport of ions in the human blood system; with a focus on the plasma (Encyclopaedia Britannica, Inc. 2014).*

The buffer of blood is intravascular liquid and the pH is kept at ~7.4 by the carbonic acid –bicarbonate ion buffering system–, but the pH of human blood ranges from 7.35 to 7.45, thus a change of 0.10 pH unit is significant. And, there is hemoglobin with respiration because it is used for medical purposes where it has been found possible to determine the percentages of dissolved oxygen, nitrogen, carbon dioxide, and carbon monoxide (GLC – Gas/liquid chromatogram) in blood samples as small as $1cm^3$. Also, most enzymes are very sensitive to pH and can function properly only in a rather narrow pH range. Even minute deviations from the norm may spell or foretell disaster and that's why the blood pH is routinely measured to one-thousandth of a pH unit.

Table 1. *Summarizing composition of buffer systems of blood.*

Summarizing the composition of buffer systems	Perceptual of total
Bicarbonate / acid carbonic	~ 64%
Hemoglobin /oxi hemoglobin	~ 28%
Acid proteins / basic proteins	~ 7%
Monoacid phosphates/diacid phosphates	~ 1%

The experimental results describe the analytical detections of the solid matrix of whalebone that contain, e.g. calcium, iron, and zinc.

Typically, natural systems are complex, and several factors

influence the bioavailability of Ca^{2+} but the pH is the main one. Like Zn^{2+} where the pH is very important and is another metal that has investigated biological systems complex; in the presence of aqueous micellar media with Ditizona and Triton X-100 and 8-hydroxyquinoline (see the next Figure) [4].

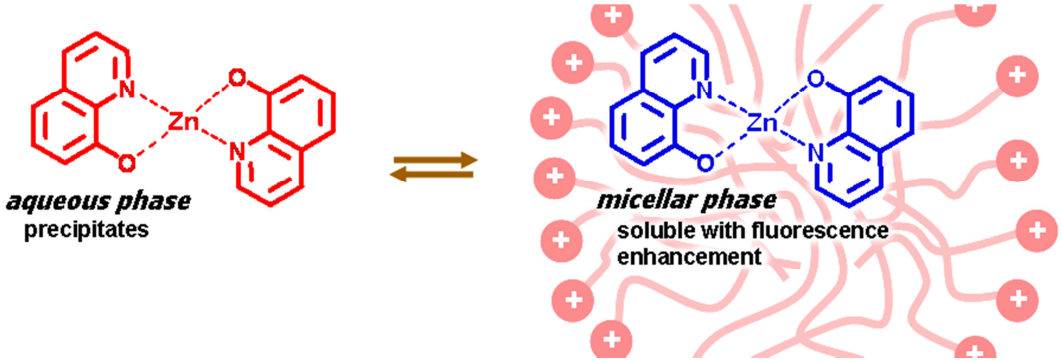


Figure 2. *Mixtures of Zn^{2+} and 8-hydroxyquinoline in aqueous solutions and micellar phase [4].*

The use of the micelles as reaction media was because the pronounced effects of organized media on a variety of ground- and excited-state reactions and equilibrium are well-known and have been investigated for several decades [5].

Zn^{2+} is very easy to determine using EDXRF; this would serve as a check test of the methodology with both Ca^{2+} and Zn^{2+}.

In the smooth muscle cells of animals, there are calcium channels in which an enzyme called calcium ATPase (see figure below) expels the excess of calcium ions from the interior liquid of the cell (the cytosol) to the extracellular compartment, transforming ATP (Adenosine-triphosphate Acid or adenosine triphosphate) into ADP (Adenosine-phosphoric Acid) consuming energy.

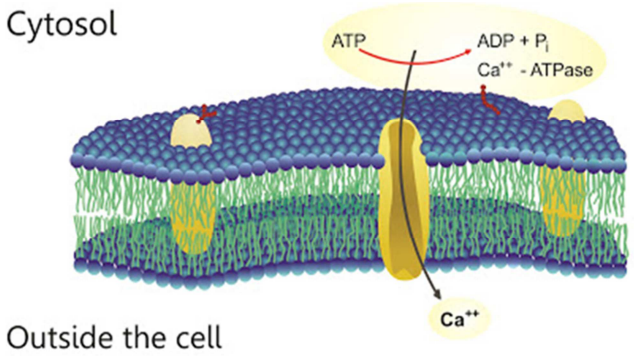


Figure 3. *Cell Membrane and the Calcium ATPase pump, which ejects calcium from the cell. A figure of the authors. See more about "Membranes " Mello et al., 2006 [6].*

If the microenvironmental conditions are ionized hydrogen free (pH^{+}) then it is favorable to have Zn^{2+}, a possible exchange with Ca^{2+} so it can be transported through to channels.

Roald Hoffman (American Scientist, 2014) explains that the "*inside of us*" works on more subtle atomic and molecular interactions that operate on energy scales 10 or 100 times smaller. Often it is not possible to calculate energies exactly, e.g. responsible even for marvelous structures, such as a cell membrane. Let's get the energy scales into focus. Energies in chemistry are measured per molecule or per mole = 6.0223 x 10^{23} molecules. A common energy unit is that of kilocalories (kcal)/ mol. It is easy to understand what a kilocalorie is since we need the daily equivalent of ~2,000 kcal on average (if that food were burned) to function. The simple phenomena of cumulative effects are hydrogen bonding at the molecular level or surface tension on a macro scale at work. The driving force for aggregation, so-called hydrophobic bonding, is qualitatively understood, but the details are very complicated [7].

This work is explored the EDXRF´s capacity to determine the ionic elements in different materials: whalebone, figuratively represented as a biochemical biomarker from Santa Catarina Island (Brazil) could be like a model of a mammal bone. Similar to the work "Biochemical biomarkers and metals in Perna mussels from mariculture zones of Santa Catarina, Brazil", in which mussels that were transferred to another, more urbanized sites (Ponta do Lessa) with shared physicochemical features to the originating farming sites (Sambaqui), were also chosen to evaluate biomarker responses to pollution [8].

The utilization of EDXRF has also marked complex reactions in the presence of metal ions which were described in cases of nanoparticles commonly applied for catalytical purposes with detail (see Figure 4 [9, 10]).

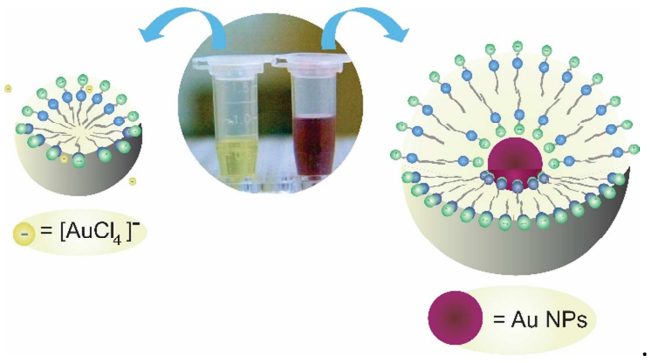


Figure 4. *Simultaneous nondestructive analysis of gold nanoparticles using EDXRF [9].*

1.1. When the Focus Is on Calcium

Calcium is found in living matter in two mineral forms:

i) in solution, in the form of dissociated ions which play important roles for cellular function, and

ii) in the form of fixed structures with little or no solubility in cell compartment secretions and the cytoskeleton. The cell's secretions can be found in the form of carbonates, phosphates (in the bones of vertebrates), or oxalates. When the salt in these secretions is too abundant, there is a tendency to sediment and create problems in cellular physiology (e.g. stones and crystals in different organs).

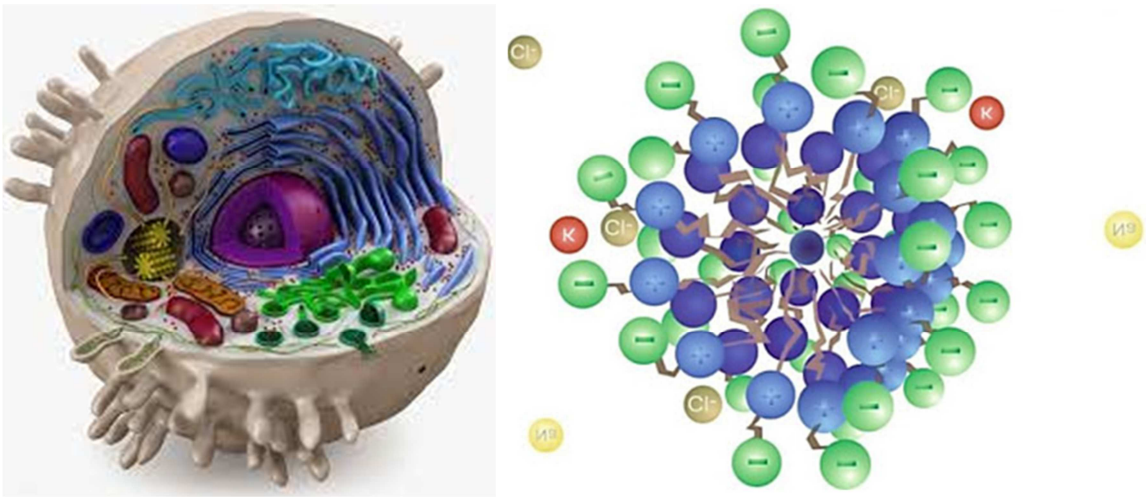
One of the most abundant mineral elements in the human body is calcium, representing between 1.4 and 2% by weight thereof. Years of scientific research have shown that calcium ion is far more versatile than its familiar role as the basic material of bones and teeth would suggest. These long research efforts have shown that the calcium ion is an almost universal intracellular messenger. The ion participates in the transcription of genes, muscle contraction, cell proliferation, and many other processes where it is crucial to control the amount of calcium in an intracellular compartment [11]. Into 1% of calcium present in the human body, most calcium (99%) is found in bones and teeth. Bone is a living tissue, but it is not renewed as we age. So, over time, bones weaken. This happens to all humans, and probably to all mammals.

Life is movement and goes through the cell membrane and the calcium ATPase pump, which ejects calcium from the cell. So, calcium could be replaced by another ligand element, for example, Zn^{2+}'s availability depends on its pH, and how it's reviewed. In addition to this, cellular calcium transport has been the subject of very careful scientific studies since it has great importance in our lives.

Many of the disastrous effects caused by ionic imbalance are because ions such as sodium, potassium, and calcium exert antagonistic effects; for example, potassium lowers the viscosity of cytoplasm, while calcium increases it.

For the understanding of the interaction processes of the calcium transport or another ion concentration, the compartment of the cell membrane could be like a compartment of a micelle. In this manner, micelles (see figure 5) serve as simple models of only the cell membrane. Chemists try to understand how these cations bind selectively in the cell wall.

In the references, it is possible to know that in some cases the ion concentration and ion relation (for example K^{+}/Ca^{++} in a compartment may differ significantly from those in the cytosol) [12].



A B

Figure 5. *A. Cells of a human being (Internet information, from August, 5th, 2022). Buffer into the liquid of the cell is intracellular. B. Micelle of a dipolar ionic surfactant. A figure of the authors. (For more see: "Chameleon Effect", [13, 14].*

It is noteworthy that the investigation of the binding of a series of ions to aqueous micelles of sulfobetaine has evidenced the so-called *chameleon effect*, in which the initial anion binding driven by electrostatic attraction to the ammonium group is followed by the incorporation of cations into the "anionic" micelles. In this sense, we are particularly encouraged in employing the zwitterionic SB3-14 as the micellar medium for the quenching of pyrene fluorescence to elucidate whether the anionic tetrachloro complex of Au^{3+} follows the same behavior observed for the other anions already investigated [14]. In this case, the authors Gerola, Wonderland, Idrees *et. al* (2020)'s focus was Au^{3+}. The fact that $AuCl_4^-$ binds strongly to the zwitterionic micelles of SB3-14 is particularly interesting for several practical reasons. For example, it points to the possibility of using such micelles as agents for concentrating anionic gold species in its recovery in mining processes of both gold and iron [15].

1.2. Study of a Case from the Reference Material: BCR-723 Road Dust

BCR-723 Road Dust (which contains the certified elements of Pd, Pt, and Rh) was used apart from the reference material as a model of charged metallic ions. Thus,

when we are dealing with solutions that are not optically transparent, such as a solid matrix of e.g. Sapphire/Al_2O_3, the use of direct sample analysis of a liquid by energy (EDXRF) is a possibility [9].

Also, another example of work using EDXRF is "Quantitative analysis of mineral nutrients in Malaysia in rice species and dietary intake assessment, a case study" [16]. At Madagascar Island, the use of the instrumentation EDXRF was successful to assess the nutritional and mineral contents of rice and its elements. Essential major elements and trace elements are quantitatively determined. The accuracy of the instrumental method and analytical procedures are checked by using the Reference Material.

Also, erbium, titanium, and silver ions were for simultaneous analysis with EDXRF. The procedure is given in "pellets" filled with a prepared mixture of boric acid or tetraborate. Total homogeny is like a ceramic material.

When the focus is a sample of dust and the origin is environmental, e.g. the initial interactions between natural water and mineral phases occur during the weathering of rock fragments that undergo modification in streams, rivers, lakes, estuaries, and eventually in the sea. The acidity of aqueous solutions determines which metal ions are soluble in it, or are hydrolyzed and, perhaps, precipitate. Consequently, the availability of metal ions, e.g. in the soil depends on its pH, which is why the soil pH largely determines which plants can grow in it. During this process, the composition of natural waters can be influenced directly by the formation or dissolution of particles or indirectly by the adsorption-desorption reaction at particle surfaces. In the case of seawater, it is very important to know that it is necessary a very careful study because there is a pH and a lot of questions like the inorganic precipitation of minerals in natural waters that is the formation of evaporated salt deposits [17].

However, an unusual and localized event, and most particulate matter produced "*in situ" is of biological origin.* It is difficult to separate living from nonliving particles, and such distinction might be misleading since biological processes often control the course of inorganic reactions in natural systems. Bacteria actively colonize detrital material and are largely responsible for degradation, while, conversely, encapsulated bacteria can act as sites for mineral deposition and the accumulation of metal oxyhydroxide aggregates [17].

There are numerous mechanisms potentially involved in this ability to buffer pH.

Some of the most important ones listed in order of the soil pH range at which they function are the carbonate mineral buffering.

2. Materials and Experimental Section

2.1. Materials, Analytical Standards, and Preparation Procedures

Aluminum titanate (Al_2TiO_5) and La_2O_3 from Sigma-Aldrich.

$HAuCl_4$ (Gold III chloride hydrate): Sigma-Aldrich, Lote MKBN2548V; Pure 99.999%.

TROX-100 Laminar Flow Hood.

Pearl or Glass disk → Sapphire/Al_2O_3 (United States of America-ISP Optics – ALHS-5/hemisphere (ISP Optics – ALHS-5/hemisphere).

The standards for measurement and testing to the European Commission were Road Dust BCR-723;

Natural Moroccan Phosphate Rock BCR-032; and

Lead Glass BCR-126.

Doubly deionized water with conductance, 5.6 x 10^{-8} Ω^{-1} cm^{-1} and pH 6.0-7.0 from a Nanopure deionization system (type D-4744) or Purelab UHQ system were used to prepare standard and reagent solutions. All other reagents were of the best available analytical grade.

All vessels in contact with samples or reagents were cleaned by soaking in 5.8 M HNO_3 (overnight) and rinsed repeatedly with de-ionized water before use.

Traceable certified reference materials from either TraceCERT or CertiPUR were used for all analytical experiments with gold and silver. Standard solutions containing 1001 +/- 3 mg L^{-1} of gold ICP-OES standard (Au CertiPUR 1.70321.0100: lot HC942080, accredited by the DKD (Deutscher Kalibrierdienst) with control of trace impurities into ug L^{-1}. Ibidem to Ag^{+}.

2.2. Instrumentation

PANAnalytical, model EAGON 2 Melting Furnace: Glass disk, pearls or lens → Synthesis of pearls: an automatic sampler and EQUA-OXIDES software application were used for instrument control, data collection, and data analysis (Bruker, Germany). Before analysis, instrument calibration and stability checks were performed.

Synthesis of the pearls: approximate quantities of 0.5g of sample and 5 g of flux composed by a mixture of lithium tetraborate ($Li_2B_4O_7$) and lithium metaborate ($LiBO_2$) in a proportion of 12:22 were weighted with an accuracy of 0.0001g directly into clean crucibles and fusions (Pt-Au-Rh) were performed in a PANAnalytical melting furnace, equipped with two positions for fusions, which are automatically flipped into Pt-Au casting plates with a diameter of 40 mm and slowly cooled. Temperature > 1250°C.

PE-MAN press: Pellet: prepared with a mixture of Boric Acid or Tetraborate. Total homogeny is like a ceramic material.

EDXRF Analysis Instrument. The EDXRF measurements were made in a temperature-controlled room (23 +/- 1°C) using an S2 Ranger (Bruker, Germany). Samples of 5 mL were placed in an XCell (with a diameter of 40 mm) and covered with a 5 µm thick polypropylene film, special for XRF analyses. The S2 Ranger measurements were carried out using a Pd X-ray tube, operated with a Cu filter and 50KV and 250 um. The acquisition times were 250 s (measurement time *per* region in the presence of air) and 150 s (measurement time per region using helium). The X-

Ray to excite the sample was produced using a 50 W, 50 KV/2 mA X-Ray VF 50tube. The tube and generator can operate at voltages ranging from 10 to 50 kV and currents from 1 to 2000 µA, providing a maximum power of 50 W that is not exceeded. An automatic sampler and EQUA ALL software were used for instrument control, data collection, and data analysis (Bruker, Germany). Before analysis, instrument calibration and a stability check were performed.

3. Results and Discussion

When the focus is calcium, it is possible to say that it is the most abundant mineral element in the human body. Into 1% of calcium present in the human body, most calcium (99%) is found in bones and teeth. Bone is a living tissue, but it is not renewed as we age. So, over time, bones weaken. This happens to all humans, and probably to all mammals.

The amount of calcium in a human cell is controlled. Minor variations in the ionic balance of seemingly simple ions such as sodium, potassium, and calcium can have disastrous effects and modify permeability, sensibility, contractility, and cell viscosity. Calcium, together with sodium, potassium, and magnesium cations, make up the main set of mineral salts in solution, controlling the pressure, the signals of nerve impulse conduction, and communication in the brain and heart. This is the target area for drugs that block calcium channels that specifically inhibit or activate the flow of calcium ions across membranes.

3.1. Procedures of Whalebone

The current technique is possible to analyze solid or liquid samples, dissolving the bone with acids according to the equation shown below.

$$Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \text{ --> } 10Ca^{2+} + 6H_2PO_4^- + 2H_2O$$

The result was 31% Ca to 13% P (of the dry weight).

The mass ratio Ca / P of 2.4 is very close to the expected value of 2.2.

About the fossils, in Oceans the opinion has long been divided as to the Mg/Ca ratio in seawater [18]. Here, it is only said that it was identified.

Analogous to the human bones we show the analysis of our model with a whalebone, found on the beach of Ponta das Canas-Florianópolis close to the Whales' channel (Santa Catarina-Brazil). The chemical composition was determined by EDXRF for this bone, buried for several years.

Figure 6 shows the summary of the action spectra of the whalebone.

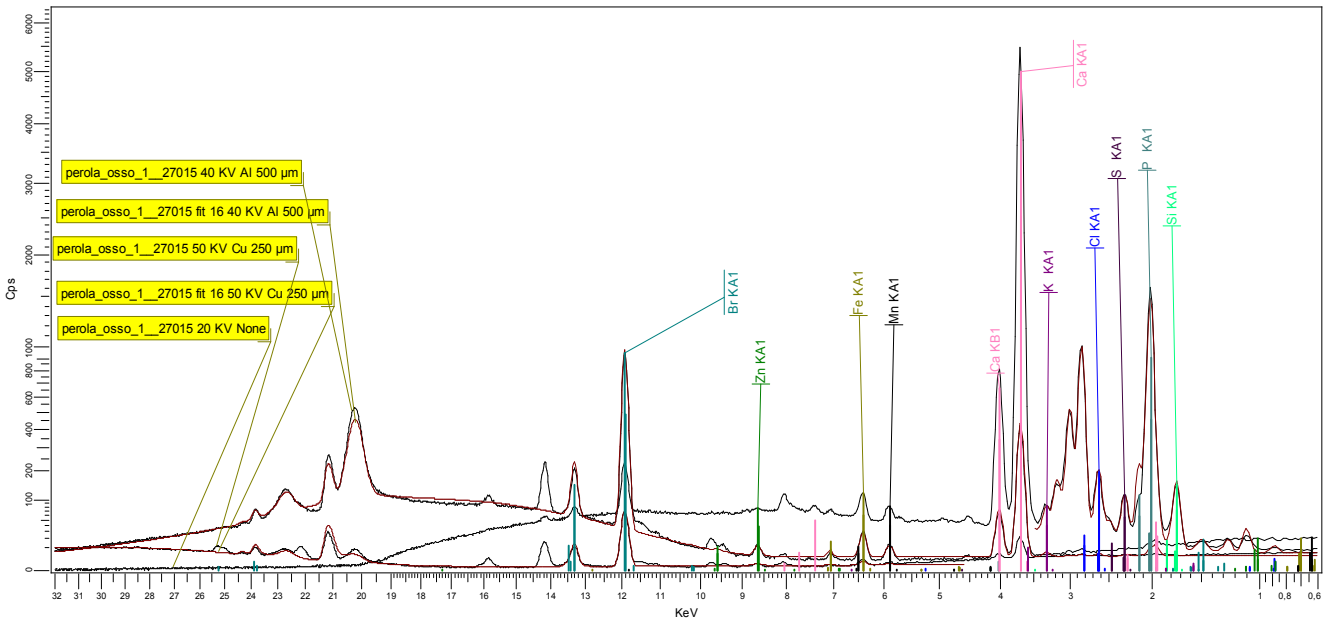


Figure 6. *EDXRF spectrum obtained from a sample of whalebone in pellet form. Ca and P are, of course, not the only elements present.*

The chemical nature of the constituents provides the basic information required to explain the modes of operation of cellular organisms. The results are of interest to professionals from archaeology to medicine.

3.2. Application of the EDXRF (X-Rays; λ~1nm) to Characterize of Ca^{2+} and UV (Ultraviolet λ~100-300nm) to Vitamin D

The example illustrated allowed us to investigate and evaluate the past, in terms of a simple bone: that was once part of a magnificent, living whale.

Bone disorders are related to disturbances in the interplay between the parathyroid hormone (PTH), calcium (Ca^{2+}), and vitamin D, ie in the Calcium-Parathyroid hormone-Vitamin D axis [19]. Rickets, e.g., due to a severe deficiency of the latter in children only, significantly affected the European population around the 1880s. Pathophysiologically, low vitamin D levels decrease intestinal absorption of calcium. Parathyroid hormone

secretion then increases to maintain plasma calcium, which causes renal phosphate wasting and impaired bone mineralization [20]. In children, rickets is characterized by excessive unmineralized osteoid matrix at the epiphyseal cartilage. X-rays show osteopenia and pseudofractures in osteomalacia (i.e, its adult version), epiphyseal widening, and metaphyseal cupping/fraying in rickets. Children with the disease have pathological bowlegs (genu varum), beadlike costochondral junctions (rachitic rosary), and craniotabes (soft skull). Risk factors include exclusive breastfeeding, inadequate sun exposure, heavy skin pigmentation, and the absence of fortified dairy (dairy alternative) foods. Chronic vitamin D deficiency can lead to adult osteomalacia [21] clinically manifested with bone pain or tenderness, muscle weakness or cramps, gait abnormalities, and increased fracture risk. This chronic form is also associated with limited UV exposure and poor diet, two poles between first and third-world nations respectively.

Vitamin D is a lipophilic vitamin essential for the development and maintenance of the skeleton. On exposure to sunlight [22]**,** 7-dehydrocholesterol (provitamin D3) in the skin absorbs ultraviolet (UV) B rays. This opens the B ring of 7-dehydrocholesterol, forming previtamin D3, which then undergoes thermal isomerization to form vitamin D3 (cholecalciferol). Vitamin D3 is then hydroxylated in the liver to 25-hydroxyvitamin D and subsequently to 1,25-hydroxyvitamin D (the active form) in the kidneys.

Severe deficiency causes rickets in children, resulting in skeletal deformities, such as "bowlegs". D3 (cholecalciferol) comes from exposure of skin (stratum basale) to the sun, and ingestion of fish, milk, and plants; D2 (ergocalciferol) from the ingestion of plants, fungi, and yeasts. Both are converted to 25-OH D3 (storage form) in the liver and the active form 1,25-$(OH)_2$ D3 (calcitriol) in the kidney [19]. Foodstuffs from the plant kingdom contain only minimal amounts of vitamin D. There are, however, flora with substantial quantities of ergocalciferol, vitamin D in D2 form. Man and higher-order animals cannot alone turn ergocalciferol into vitamin D, but such a reaction can occur with the aid of UV light. The conversion can be made to proceed by irradiation of a solution of ergocalciferol. An analogous process takes place in the human skin.

Osteoporosis, a condition characterized by the presence of brittle bones and a tendency to fracture, is frequent among the elderly. The term means porous bone, from Latin *spongiosis*, that is made of minerals and other inorganic materials similar to hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, which is deposited along collagen fibers. In contrast to hypocalcemic disorders, this condition is characterized by loss of trabecular (spongy) and cortical bone mass despite normal bone mineralization and lab values (serum Ca^{2+} and PO_4^{3-}). The pathology results from an increase in bone resorption due to more and more active osteoclasts [23] (ie, cells responsible for bone cleavage) in the appendicular skeleton, and is related to low estrogen levels and advanced age. To prevent fragility fractures, prophylaxis through regular weight-bearing exercise and adequate Ca^{2+} and vitamin D intake throughout adulthood is recommended, particularly in postmenopausal women.

The humble and hidden atom of phosphorus (P) is a key component of the genetic material of all living beings. Bacteria, viruses, and mammals share phosphate-containing groups as the "spine" to which the nucleic acids responsible for the storage (DNA) and transmission of genetic information (RNA) are attached. As if all these functions were not enough, its inorganic form represents an important biomarker in bone disorders.

Bone is continually broken down and reformed by the process known as bone remodeling, which consists of the coordinated activity of osteoblasts (responsible for bone formation) and osteoclasts (responsible for bone resorption). Osteoblasts, aka "bone builders", synthesize the matrix and express alkaline phosphatase (AlkP), an enzyme promoter of normal bone mineralization by increasing local concentrations of inorganic phosphorus. Serum AlkP levels correlate with osteoblastic activity. Therefore, hypovitaminosis D, a hypocalcemic disorder *per se*, is accompanied by low PO_4^{3-}, a consequence of the increased levels of PTH secreted by the anterior pituitary to compensate for their lack [20].

PTH is one of the six major hormones released by the *anterior* pituitary gland, which still has a *posterior* division. The release of PTH occurs in response to low plasma [Ca^{2+}], high plasma [PO_4^{3-}], or low plasma 1,25-$(OH)_2$ D3. As a rule, PTH causes more [Ca^{2+}] reabsorption, less [PO_4^{3-}] reabsorption in the kidneys, and more 1,25-$(OH)_2$ D3 production (increased Ca^{2+} and PO_4^{3-} absorption from the gut via vitamin D) [24]. The biochemical interplay of these reactions is not here to be discussed in further detail but their biological role could only be made possible to "*corticalize*" and reach the human consciousness through the extensive years of research and development in hard sciences.

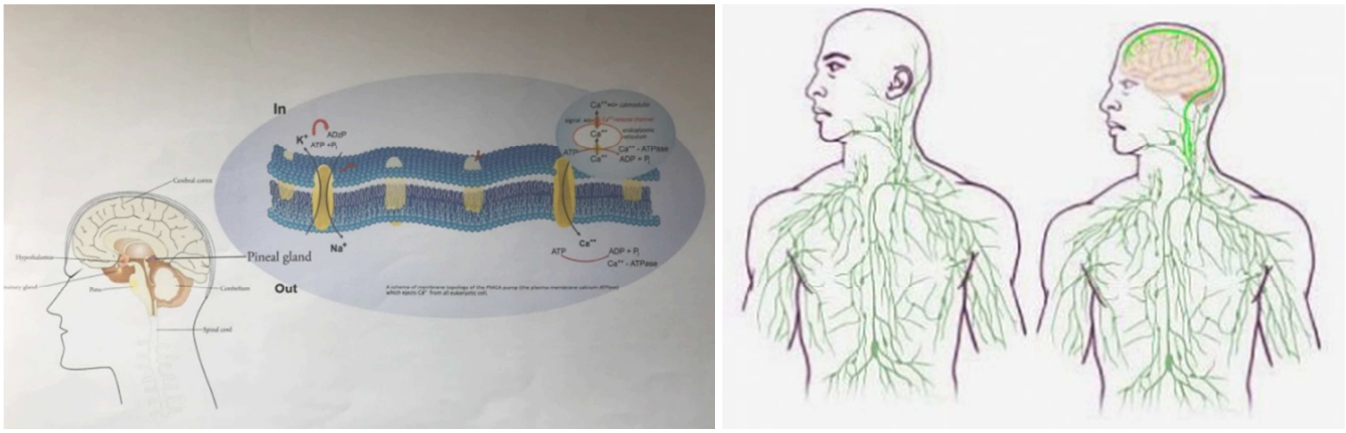
There's no doubt at this point that the weak interactions through which the phospholipids maintain basic cell membrane structure are far more complex than their humble name may imply allowing the formation of this superstructure to cells, the essence of life. With organic phosphates, more dissolved calcium salts are dissociated into ions, and the control of the concentration of these ions intracellularly involves specific physiological pathways, which require energy consumption. In addition, main organic phosphates are still responsible not only for the transport of energy (ATP) but even to ensure the functioning of memory and proper cell signaling between nerve fibers and tracts. [25, 26].

The pituitary gland is a major receptor of signals from the hypothalamus to the secretion of hormones. Although most phosphorus in the body is in the form of hydroxyapatite in bone, circulating phosphorus is primarily in the form of phosphate/phosphoric acids. Interestingly, bisphosphonates (eg, alendronate, risedronate) are pyrophosphate analogs that attach to hydroxyapatite binding sites on bone surfaces and

inhibit osteoclast-mediated bone resorption [27], characterizing their role as a pharmacological therapy for osteoporosis.

To illustrate the impact of hard sciences in clinical practice a simple experiment could be performed through analysis with EDXRF methodology, the precipitation of calcium into apatite in the epiphysis, regulator of the circadian rhythm. For this experiment, a high concentration of Ca^{2+} and nucleation (see Figure 7A) only would be required. The effects of irradiation are *a priori* physical but can modify biological functions in intricate and seemingly unpredictable ways. Studies in mice [28], eg, suggest that pineal-derived melatonin regulates new bone deposition in an underexplored pathway which could be a potential new target for osteoporosis treatment.

In Figure 7B the human lymphatic system can be seen and analogously compared to the model of compartments, ie, of channels branching into many other channels, used in this paper, which may seem to occur in mysterious ways despite being distributed according to the constructal law [29].



A B

Figure 7. *A. Localization of Hydroxyapatite in the human brain Figure of the authors. B. Schematically drawing of the method used in our model of compartments into many channels of the human lymphatic system (https://www.nih.gov/news-events/nih-research-matters/lymphatic-vessels-discovered-central-nervous-system).*

The Ca^{2+} can also be vile and has been associated with the incrustation of arteries of the cardiovascular system. Doctors and dentists often perform X-ray analyses of our bones and teeth. This imaging technique is based on the amount of calcium present in the respective tissue as its cellular loss is translated, eg into porosity and other modifications. Chemists make use of the same technique to determine the elemental composition of a bone, most often in solid form.

In the present work, the option was to use whalebone.

In Medicine, for the tissue to properly adhere to an implant, such as in a stainless-steel hip replacement, a coating must cover the implant. Hydroxyapatite might be also represented by $Ca_5(PO_4)_3(OH)$, a mineral component of teeth and bones that is applied through a plasma spray process as a bioceramic providing good tissue adhesion to the implants [30].

3.3. Application of the EDXRF to Characterize Ions of Mineral Material of the Real Dust

The elements Fe, Ca, Al, and Si are present in compositions of clay minerals, for example, kaolinite and montmorillonite [31]. Motor fuels consist of gasoline, diesel, jet fuel, and liquefied petroleum gas (LPG-mainly butane). Cars use essentially gasoline or LPG, whereas trucks use mostly gasoline (85% gasoline and 15 diesel as a consumption basis).

The correct characterization of metallic elements in air filters (there are various mechanical particulate collectors of road dust) is of paramount importance since it gives information about its quality (as a metallic element deposit) but also about the origin and effects of various anthropogenic activities. Today's emerging technologies may very well become tomorrow's conventional technologies because engineers and scientists continuously improve upon these technologies.

As they increase in numbers, humans are using technology to hit higher standards of living. As a consequence, we continue to modify the atmospheric composition, water quality, and land surfaces, as well as introduce metals, transition elements, and lanthanides into the environment.

Therefore, the results are present in Table 2, and in Figure 8 (EDXRF spectra) it is possible to observe the results of the semi-quantitative chemical composition of the samples of CRM – Road Dust (BCR-723), indeed it can be seen that these results are indicative of the elements present in soils are present at measurements of EDXRF (Si> Ca> S> Al> Mg> Fe> K). The concentration of $[SiO_2]$ = 23,9 reports a characteristic acid. Not from "volcanic dust, where the SiO_2= 67.14%.

The elements Ti, Zn, Pb, and Cr probably have an anthropogenic origin. The same is in the case of Fe and Mn oxides present in sediments of CRM-601 [32].

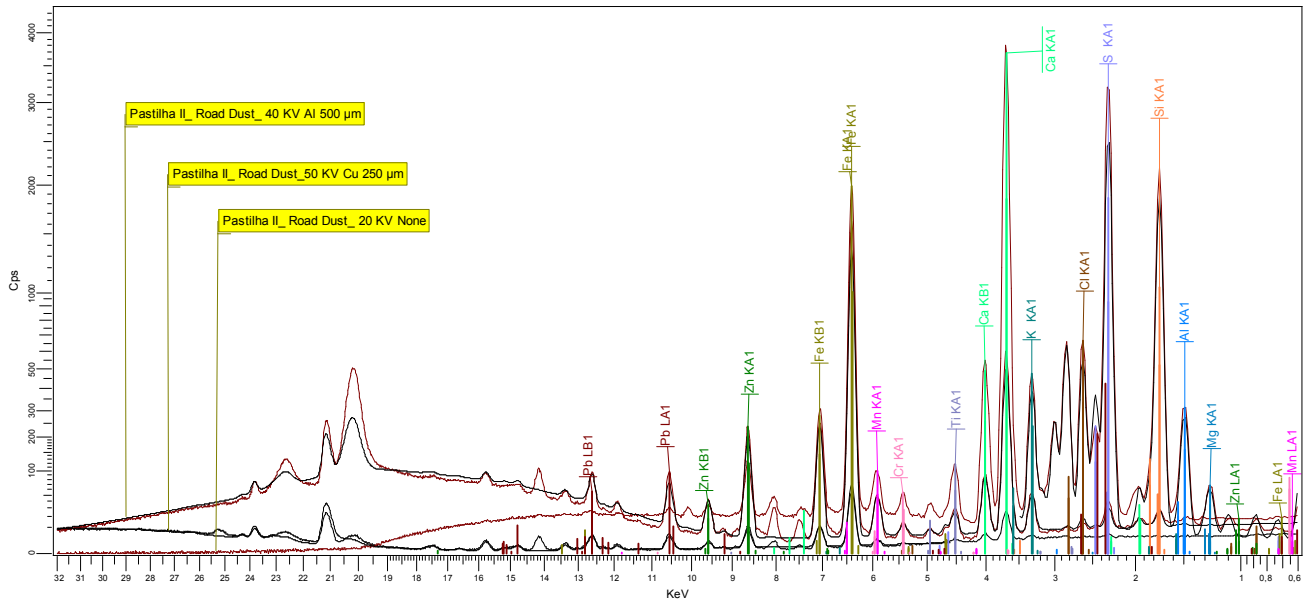
The fossil combusts (coal) is very similar [33]. So, much more like the case of total particulate matter, the measurements of the elements.

Table 2. *Semi-quantitative chemical compositions (%) of samples of CRM –Road Dust (BCR- 723).*

	SiO_2	CaO	SO_3	Al_2O_3	MgO	Fe_2O_3	K_2O	Cl	TiO_2	ZnO	MnO	PbO	Cr_2O_3
%	23.9	13.7	11.6	8.3	4.9	3.8	4.9	1.3	0.4	<0.2	<0.2	<0.1	<0.1
SD	0.3	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	-	-	-	-

SD = Standard Deviation. n=2
LOI =25.4 +/- 0.4 (Loss to Fire = mainly H_2O and CO_2).

Figure 8 shows the results of the semi-quantitative chemical compositions of two samples analyzed independently. Three types of determination: with 40 KV and filter Al 500 µm, 50 KV and 250 µm, and only 20 KV. And it is possible to know the interference lines if the interest is the determination of one element, the example is the case of Erbium (see Table 3).



LOI = 25,4 ± 0,4 (Loss to Fire = mainly H_2O e CO_2).

Figure 8. *EDXRF spectra for the semi-quantitative analysis (pellet form) of CRM – Road Dust (BCR® 723). The energies were determined independently with: i) 20 KV, without a filter; ii) 50 KV, with a Cu 250 µm filter; iii) 40 KV, Al 500 µm filter.*

According to the results of the European Commission Certification, reference measurements of the reference material are present in Pd, Pt, and Rh. For instrumentation EDXRF the possibility of determination of these elements would be done with the same procedure that in the case of gold and silver, see Figures 9 and 10. Also, the element Lanthanum from La_2O_3 (element of transition intern-*f* with / lines$_{\alpha 1}$; $L_{\alpha 1}$; $_{\beta 1}$) using $Li_2B_4O_7$ (see Glass disk *pearls or lens* at Instrumentation).

The elements Au, Rh, Pd, Ti, and Er were determinate for us and presented in other works [9].

As a decision, if the analysis will be prepared with an aqueous solution, pearls or pellet is to know the interference of Erbium, for example, it is necessary and possible to know the possibilities of interference lines [10].

Table 3. *Erbium and the interference lines [34].*

Element	**Er^o**	**Co^o**	**Er^o**	**Cu^o**
Energy line	$L_{\alpha 1}$	$K_{\alpha 1}$	$L_{\beta 1}$	$K_{\alpha 1}$
Energy (keV)	7	6,9	7,8	8

L_α = particle α; L_β = particle β (internal electronic conversion)
KeV = power of charge electron or energy, tension)

About Erbium and Cobalt, the difference in energy is only 0,1 KeV, so it is possible to occur the overlap of lines. The same happens in the case of Erbium and Copper, the difference in energy is only 0,2 KeV. So, the first step is to do the semi-quantitative of the sample to identify the lines of interference (if the presence of elements with so close a difference of energy).

There is a "Periodic Table of the Elements" with the Bragg angle, all spectral lines, and energy (KeV). For example, calcium => $K_{\alpha 1.2}$; $L_{\beta 1}$; $L_{\alpha 1}$ and $L_{\beta 1}$.

The electronic configuration is also important to know.

From this idea, by measuring the wavelengths of light emitted from different kinds of atoms, it has been possible to gain an understanding of the structure of another part of the atom, the electron shells. The whole science of *atomic physics* was founded almost exclusively on this *spectral analysis.*

3.4. Application of the EDXRF to Characterize Ions in Aqueous Solutions

Concerning the aqueous solutions, it is possible to prepare and determine how it is proposed in a more sophisticated work with nanoparticles [9] or a certified sample aqueous solution can be used. However, in such cases, the matrix background of problems would require pairing with the match matrix (Figure 9).

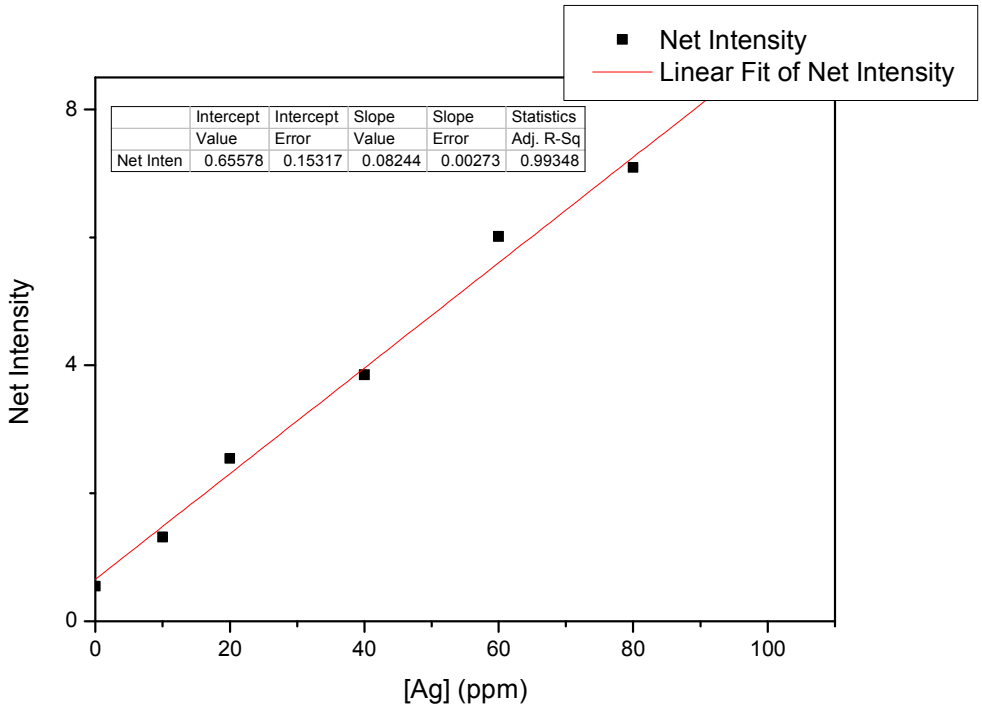


Figure 9. *EDXRF intensity as a function of the concentration of a certified Au^{3+} aqueous solution (mg/L).*

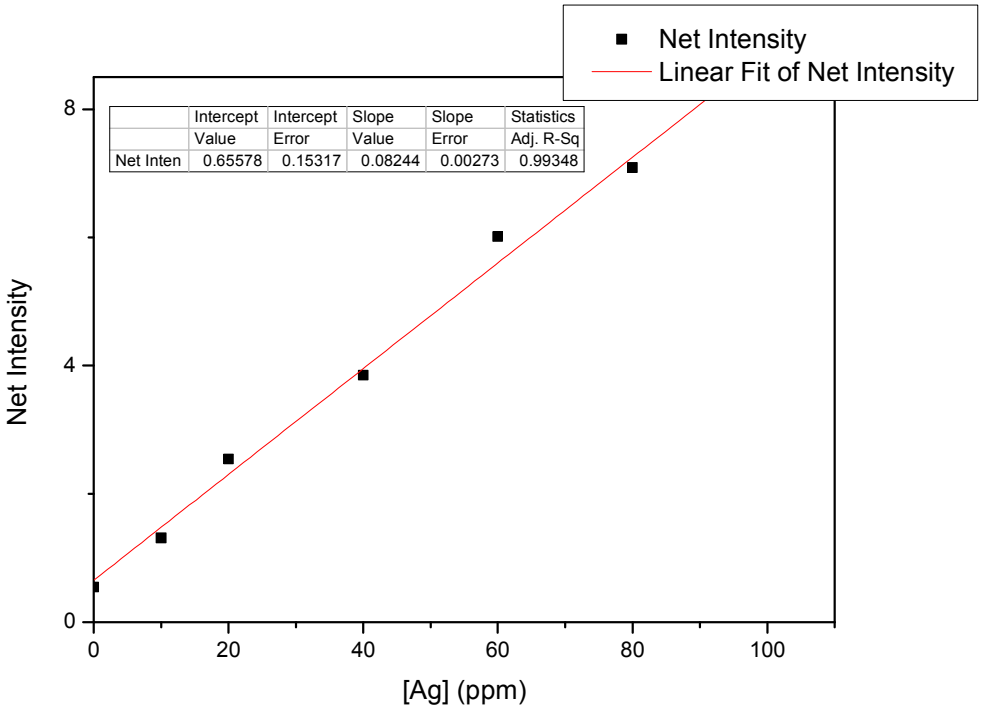
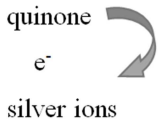


Figure 10. *EDXRF intensity as a function of the concentration of a certified Ag^{+} aqueous solution (mg/L).*

The solution of Ag^{+} is very useful in the Sol-Gel preparation of Silica Gel Sensors. Electric induction generators are used in many areas, as an alternative to energy generation because of the low maintenance cost and ease to build characteristics. There are many experiments in laboratories to produce batteries for electric cars [35]. In the

case of Ag^+, it is impossible no review the example of the *developing process of a photographic film*. In the film there are silver ions, Ag^+, and in the developer hydroquinone ions, $C_6H_4O_2^{-2}$ (or other similar substances):



Conceptually two steps; oxidation and another reduction process. The electrons (e^-) do not exist freely for any length of time but are immediately taken up by silver ions. The visualization of the redox reaction is described as a "waterfall" of electrons from a "high" container (quinone) to a "low" container (silver ions). In this "fall" energy is released, either as heat or in some other form.

Now, returning to the catalyst system in the last years, it is very important to point out that Pd, Pt, and Au are metals that are resistant to corrosion. Pt or Pd-based catalysts currently used in automobile exhaust cleanup are inactive below about 200°C. Gold-based catalysts present a potential solution to this cold-startup problem, however gold nanoparticles have been perhaps the most widely studied [36, 37].

Pd, Pt, and Rh are present commonly in metal catalysts [29] to automobile exhaust and another possibility of their reaction is to transform CO, NO_x, and HC to end into CO_2, H_2O, and N_2. The emergence of a growing desire worldwide to take positive actions to restore and protect the environment from the degrading effects of all forms of pollution, for example, air, solid waste, and water.

The total amount of carbon dioxide gases (Global Warming Gases) produced by the United States will be significantly reduced when these fuel-cell-powered automobiles vehicle are commercially available (at an affordable price) because there will be only water as a final product [37].

The current trend toward reducing the number of automotive pollutants is to encourage the use of smaller vehicles, which can give more miles per gallon, and to develop new nonpolluting vehicles using fuel-cell technology.

Toyota Motor Corp. developed a fuel-cell hybrid sports utility vehicle that has an electric motor rated at 109 hp and powered by nickel-metal hydride batteries and a hydrogen fuel cell. It also recharges the batteries which is common to see at the University of California (Irvine and Davis) reported in 2004 [38]. Honda Motor Co. has also developed a fuel-cell vehicle with an electric motor rated at 80 hp powered by a fuel cell. The EV-Plus uses a supercapacitor instead of a larger, heavier battery to store some electricity for use during bursts of acceleration. Daimler-Chrysler´s fuel-cell car is the NECAR 5, which is based on Mercedes-Benz A-Class. The NECAR 5 extracts hydrogen from methanol, a method that the company says takes up less space than pure hydrogen.

In Brazil, electric and hybrid vehicles are ahead of conventional vehicles representing almost 60% of the automobile fleet until January 2022 [39].

4. Conclusions

The examination of the results of this work revealed that the EDXRF methodology, with the semi-quantitative approach, has the utility of identifying all elements in whalebone from Santa Catarina Island (Brazil) and could be used as a model (~biomarker) to explain the interactions of Ca^{2+} and the concentration of ions simultaneously: Cl^-, Zn, Br, Fe, Mn, Ca, K, S, P, and Si. However, these ideas were initially proposed for the use of spectral lines of Ca^{2+} found in complex matrices. Because the conditions of hydrogen-free (pH^+) are favorable to have Zn^{2+}, however, much more is needed to say it is possible for the Zn^{2+} to change with Ca^{2+} and to move inside and outside of mammal cells.

Experiments involving the interaction of electromagnetic radiation with matter have provided detailed knowledge of processes that occur in atoms and molecules. Hence, the results of this work revealed that the EDXRF has utility in the identification of all elements certified into Road Dust (BCR-723) and that it could be a good model for charged ions. For example, the case of dust, soils, sediments, fossils fuel, ceramic, and bio-ceramic.

The therapeutic use of gold compounds is of considerable antiquity. It has been used for the treatment of patients undergoing chrysotherapy for rheumatoid arthritis for years and here the methodology EDXRF again showed itself useful in studies with Au^{3+} applied with a matching matrix.

To Ag^+ the use of EDXRF would be possible (with a matching matrix) in the case of the studies of solution of Ag^+ into the Sol-Gel preparation of Silica Gel Sensors for laboratories to experiment and produce batteries for electric cars.

The results with certified samples of ROAD DUST (BCR-723) and its reference standards serve as a basis for studies of aluminum oxide nanocatalysts containing Ti, La, and other elements.

Certificate Reference of Material

Sapphire/Al_2O_3 (United States of America-ISP Optics – ALHS-5/hemisphere (ISP Optics – ALHS-5/hemisphere).

The standards for measurement and testing to the European Commission were: Road Dust BCR-723;

Natural Moroccan Phosphate Rock BCR-032; and Lead Glass BCR-126.

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