The Association of Tooth Lead Content in Ancient Egyptians and Contemporary with Dental Health Factors Via LIBS Technique

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Abstract: Human calcified tissues, namely bones and teeth, have been found to be excellent "archives" related to living habits, nutrition, pollution, diseases and mobility of the ancients as well as modern human .So determinations of elemental levels in teeth can insight of the diagnostic and etiology of various diseases of ancient and recent Egyptians. Lead content was analyzed in enamel of the teeth from human Egyptian mummification dated to (1085 BC) from Sakkara area, also recent extracted sound teeth from population of the same area. Element was determined using laser induced breakdown spectroscopy (LIBS) technique. The elemental content was determined using the observed LIBS spectra. The obtained results showed an increase in Pb content concentrations in ancient Egyptians teeth more than contemporary Egyptians teeth. These results concluded that the increase of lead concentration in ancient Egyptian teeth reflects direct exposure to this elements and increasing the pollution at that period.

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1. Introduction

Lead is one of the first discovered and widely known metals commonly encountered in the environment.[(1)] Lead poisoning is one of the foremost environmental health threats.[(2)] levels of lead contaminated dust from its continued release into the environment as an exhaust emission product of leaded Gasoline, as well as due to its wide spread industrial use (deteriorated lead-based paints and lead-contaminated soil). Immediately after absorption, lead enters into the blood, which is then distributed particularly to the liver and kidneys, and is then stored in the bones and cause damage of liver, kidneys, heart, male gonads and affects immune and nervous system.[(3)] Millions of children have enough lead in their blood to reduce intelligence and attention span, cause learning disabilities, and damage permanently a child's brain and nervous system.[(4)]

It has been reported that the concentration of lead in teeth can be used as an index of environmental pollution.[(5)] Lead is preferentially incorporated and stored in calcified tissue such as teeth[(6)] and a tooth lead concentration above 4 mg/kg has been suggested as indicating a toxic body load.[(7,8)] Dental tissues are very hard and stable, allowing the heavy metals that are obtained from mineralization to be retained over time. Lead is incorporated and stored in calcified tissues, such as the teeth.[(9)]

Enamel lead indicates exposure during in utero life and first post partum year, while lead in dentin indicates exposure after the tooth development.[(10)] Lead can be accumulated in baby teeth until they shed and it can accumulate in permanent teeth while their presence in the mouth.[(11)] Teeth has an advantage over bones as biopsy tissues: they are easy to collect and are physically stable. There is evidence that teeth are superior to bone as an indicator of cumulative lead exposure because the losses from teeth are much slower as there is no turnover of apatite in teeth, as in bone, hence teeth are the most useful material for studying total past lead exposure.[(12)] Human teeth, both deciduous and permanent, are useful indicators of lead exposure of recent and historical populations. Elemental composition of the body tissues has been also used to reconstruct the dietary habits and environmental conditions of extinct population. Modern paleoanthropological research increasingly uses chemical and physical methods to analyze bone material to broaden and complement information and knowledge on the biological conditions of human groups, prehistoric diets, and the etiology of various diseases.[(10)]

Enamel, unlike other human tissues, has special property: its composition is fixed, and this could provide a historic record of trace elements absorbed during early development stages.[(11)]

We will primarily focus our study on the application of laser induced plasma spectroscopy (LIBS) to the analysis of important minerals and potentially toxic elements within teeth, Determination of elements levels in teeth on one hand gives us complement knowledge of the diets, diagnostic, etiology of various diseases and on the other hand provide us with information about the environmental conditions of ancient Egyptians in different eras.

2.Materials

Source of samples

The study included 100 samples of adult's skulls belonging to new kingdom in ancient Egyptians. These samples were excavated from the archaeological area of Sakkara. **Fig. (1).** One hubersnderd contemprarey individuals have been subjected to this study. The recent samples were extracted from individual living in the same area **(Fig.1).**

All the samples were subjected to clinical examination.

Fig. (1): Showing different sample of teeth (new kingdom and contemporary teeth)

Methods:

Preparation of teeth:

The teeth were washed with de-ionized water then dried and coded. The recent samples were scraped, washed with de-ionized water to remove any traces of soft tissues or calculus deposits, then dried.

Analytical method and scientific devices used, Laser Induced Breakdown Spectrometry (LIBS) technique, The experimental setup:

A block diagram of the LIBS experimental setup is shown in **Fig. (2).** Laser induced plasma is obtained using a Nd: YAG laser (Surlite I, Continuum, USA) delivering 7 ns laser pulses at its fundamental wavelength (λ = 1064 nm) with adjustable repetition rate up to 10 Hz (i.e. 10 pulses per second). The laser pulse energy was adjusted by a suitable combination of beam splitters, as an external attenuator at constant operating high voltage (1.3 kV) to ensure spatial beam profile stability. An energy meter (NOVA, Ophir Optronics Ltd., USA) was employed to monitor the shot-to-shot pulse energy. Plasma production on the tooth surface (i.e. on the enamel) was attained via a quartz plano-convex lens of 100 mm focal length. A 1m length fused silica optical fiber mounted on a micro *xyz*-translation stage (not shown in the figure) is used to collect the emission light from the plasma plume and feed it to an echelle spectrometer (Mechelle 7500, Multichannel instruments, Sweden). The echelle grating spectrometers, designed for operation in high orders and high angles of incidence and diffraction, can provide high resolution in a more compact size and cover a much wider spectral range than conventional grating spectrometers. The Mechelle 7500 provides a constant spectral resolution of 7500 corresponding to 4 Pixels FWHM (Full Width at Half Maximum), over a wavelength range 200-1000 nm displayable in a single spectrum. A gateable intensified CCD camera (DiCAM-Pro-PCO Computer Optics, Germany) coupled to the spectrometer was used for the time resolved detection of the dispersed light. The gating of the camera and the timing for spectral data accumulation were controlled via a PC.

The overall linear dispersion of the spectrometer-camera system ranges from 0.006 (at 200 nm) to 0.033 nm/pixel (at 1000 nm). To avoid electronic interference and jitters, the intensifier high voltage was triggered optically. The ICCD camera control was performed via special Multichannel Instruments software. Echelle spectra display, processing and analysis were done using 2- and 3-D Gram/32 software programs (National Instruments, USA). In addition to the atomic database used by the mentioned software, spectral lines identification was checked by the most up-to-date electronically published database. The experimental equipments and its working conditions are summarized in **Table (1).** All measurements were performed in air under atmospheric pressure. Five single spectra have been accumulated for each tooth at five different positions on the sound part of the tooth. The averages of the 25 spectra acquired represent the enamel spectrum of such tooth.

3. Results and Discussion

Here we report on the application of laser induced breakdown (LIBS) to the analysis of important toxic elements within enamel.

Qualitative analysis **Fig. (3)** shows a typical qualitative LIBS spectrum for human dental enamel sample using the LIPS++ program. This spectrum is the average of 20 single spectra recorded at 2.5 s delay time and 10 s gate width the panoramic Echelle spectra in the spectral range 200 - 800 nm show the UV-visible emission lines of calcium as a major element and the emission lines of Al, Ba, K, Li,Sr, Pb, Fe, Mn.

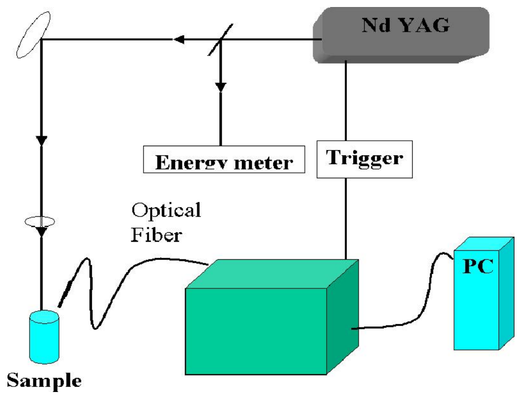

Fig. (2): Showing set up block diagnram

Table (1): The experimental equipments and its working conditions

Laser	Continuum Surelite I Nd :YAG(Santa Clara, Ca, USA)
Laser pulse	1064 nm, 100 mJ, 7 ns, 6 mm diameter
Mirror	25 mm diameter, 99%R at 45o high energy, 1064 nm, (Newport, Irvine, Ca, USA)
Lens	10 cm focal length, Plano-convex quartz, (Newport, Irvine, Ca. USA)
Spectrometer and Detector	Mechelle 7500: ICCD Camera, DiCAM-PRO (PCO Computer Optics, Germany) with echelle spectrometer and Mechelle software (Multichannel instruments, Stockholm, Sweden).
Data Analysis	GRAMS/32 version 5.1 Spectroscopic Data Analysis Software (Galactic Industries, Salem, NH, USA).

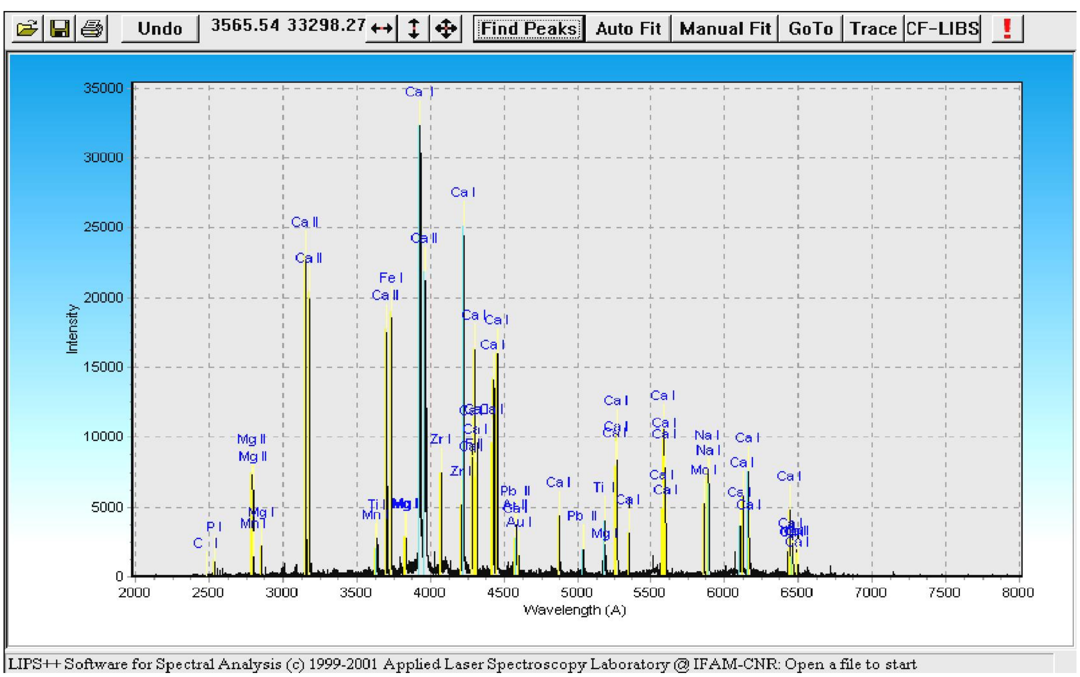

Fig. (3): Typical qualitative LIBS spectrum for enamel elemental composition

The Nd: YAG laser energy was 100 mJ at wavelength 1064 nm, plasma emissions are accumulated with delay 2.5 s, and gate width 10 s. Figure 2: Typical qualitative LIBS spectrum for enamel elemental composition. The Nd: YAG laser energy was 100 mJ at wavelength 1064 nm, plasma emissions are accumulated with delay 2.5 s, and gate width 10 s. Mg, Mn, Na, Pb and Sr as trace elements in the dental enamel sample. The observed spectrum reflects the wide spectral range and the high resolution of the used spectroscopic system.

Quantitative analysis

For quantitative elemental analysis Pb have been chosen because of their importance related to the medical, biological and environmental exposure. In order to obtain quantitative calibration data, we have used calibration curves of **Samek *et al.*(2000)** [13] obtained by fabricated arti- ficial reference samples

CaCO3 to resample the teeth enamel (hydroxyapatite $Ca_{10}(PO4)_6(OH)_2$ using LIBS technique under experimental conditions similar to ours. These were made in the form of pressed pellets of $CaCO_3$ (as the base matrix material) spiked with known amounts of Al, Sr and Pb. Thus A1, Sr and Pb were added simultaneously to the pellets, to reduce the number of individual samples and to allow for cross-calibration. The relative element concentrations were adjusted in the range 100-10000 ppm relative to the Ca content of the matrix as shown in **Table (1)** using the obtained calibration **Fig. (4)** curves and their corresponding calibration equations, the elemental concentrations of Al, Pb and Sr were obtained in the 150 teeth samples (50 for old kingdom, 50 for middle and newly kingdom and 50 for recent individuals). Then the average concentration of an element for each group (i.e. 100 teeth) represents as a column in histogram figures (5). In these histograms, a comparison of the obtained concentrations for each element in the three age categories is discussed separately as follows.

Fig. (5): shows the lead percentage variation in enamel that decreasing from the old kingdom gradually down to the recent age. These obtained results revealed the increase of the lead levels in ancient Egyptian new kingdom more than contemporary at the same area.

Our results are in agreement with the results of **Attramadal and Jonsen**[14] who found a higher lead content in Bronze Age teeth. They obtained these results from archaeological burial sites which attribute to the use of glazed pots with high lead content by ancient people. Moreover our obtained results agree with the results of **Reitznerova *et al.***[15] who found Lead content in Bronze Age is as same as in the contemporary teeth. These obtained results may be explained as follows; - Firstly, Old Egyptian used lead in many applications like small statues[16,17] load for net fishing.

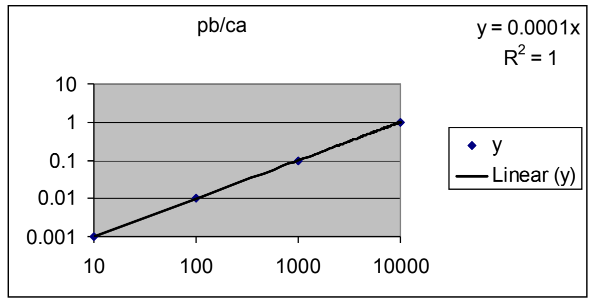

Fig. (4): Calibration curves of pb, relative to Ca

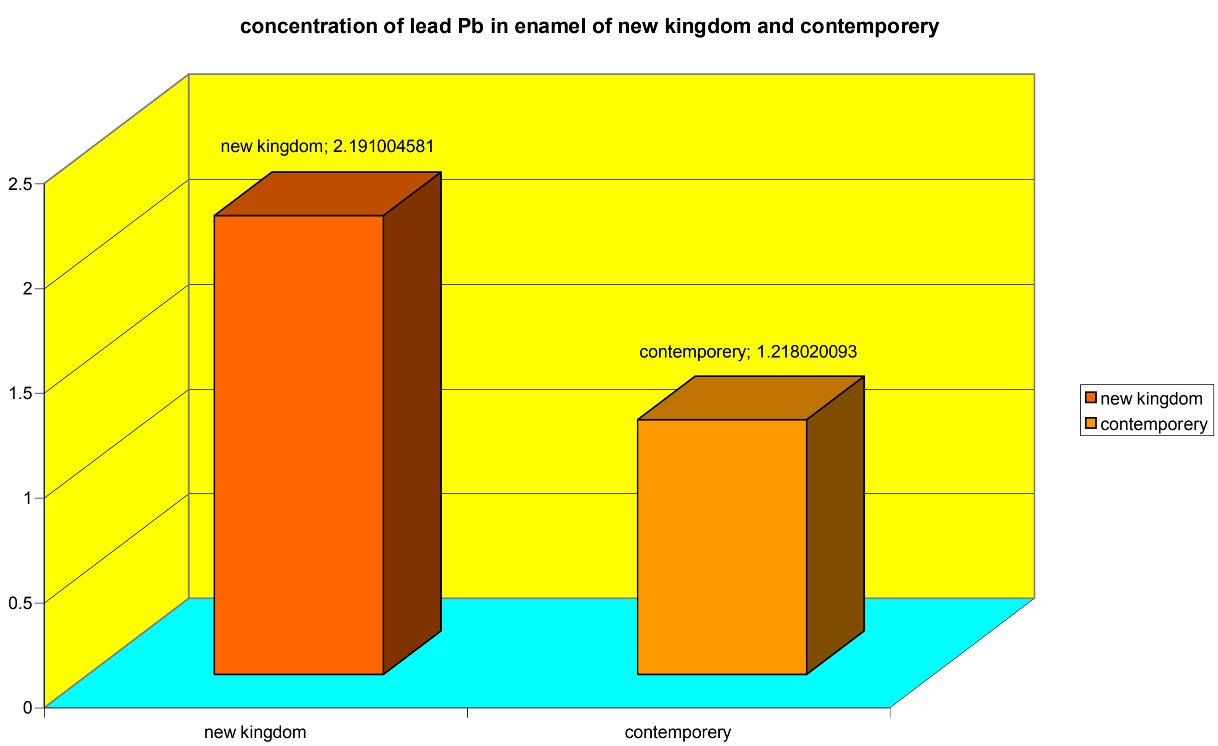

Fig. (5): Shows the Lead percentage variation in enamel that decreasing from new kingdom gradually down to contemporary

Ring, necklaces and special coating inner surface of dishes and pots, furthermore lead oxides have been used in ancient ages for painting in three ways

1. Using red lead oxide for painting some walls of Greece and Romans periods.[18]
2. Red lead oxide found on painted wall suggested to be in late period.[(18)]
3. Yellow lead oxide on painted wall suggested being 400 B.C.[(19)] Secondly, in the period from middle ages till the eighteen dynasties the most of lead products were extracted only from Egypt, not form other countries like Syria until building the Egyptian Emperor so that according to review of literature , lead was used from oldest Ages (before dynasties) till late period with viability of high level in old kingdom with little decrease new kingdom. - Thirdly, Recently ages lead is mostly used only in area of industrial application. So that lead pollution at industrial cities may give high record in environment therefore affect human being. On the other hand, in country side area (like Sakkara), the effect of lead pollution is minimize and give a little record as we found in our measurements. This is because Sakkara is away from the source of lead pollution like industries and high traffic ways.

Conclusion

Elemental analysis for Pb, was undertaken in dental enamel of 200 teeth samples for Egyptians of new kingdom to contemporary adopting LIBS technique. It is concluded that the difference in the concentrations of the studied trace elements Pb in enamel of ancient Egyptian and contemporary teeth, indicates differences of their environmental effects, especially the diet of both populations also increasing the pollution in ancient Egyptians (new kingdom) more than contemporary.

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