J Biochem Tech (2010) 2(5):S106-S107
ISSN: 0974-2328

Study of elemental distribution in urinary stones by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

Katerina Proksova, Karel Novotny, Jozef Kaiser, Michaela Galiova, Tomas Vaculovic, Viktor Kanicky*

Received: 25 October 2010 / Received in revised form: 13 August 2011, Accepted: 25 August 2011, Published: 25 October 2011

Abstract

Bio–mineral structures, i.e., bones, teeth or kidney stones have been found to be excellent "archives" related to nutrition, living habits and exposure to changing environmental conditions. More specifically, formation of urolithic concrements (uroliths) represents specific biomineralization of living organism. Line scans of the concrement cross–sections may provide information about the accumulation history of the elements of interest.

Analytical methods which can map the presence of different elements are e.g. Laser Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA–ICP–MS). Both of these methods have proven to be suitable for mapping the matrix elements, so further work is concerned with their use for the mapping of trace elements.

Keywords: LA-ICP-MS, urinary stones, distribution, major and trace elements

Introduction

One of the subjects in biomedical research is to determine the content and distribution of individual elements in human tissues. The main objective is to explain the mechanism of accumulation of selected elements in various organs, which can cause diseases and disorders of these organs.

Katerina Proksova, Karel Novotny, Michaela Galiova, Tomas Vaculovic, Viktor Kanicky*

Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Jozef Kaiser

Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2896/2, 616 69 Brno, Czech Republic

*Tel: +420 549 494 774, Fax: +420 549 492 443
E-mail: viktork@sci.muni.cz

Creation of urolithiasis is one of most common human diseases, usually with very unpleasant and painful syndromes, as they may find difficulty in urinating, and small fragments of blood in the urine (Sperrin et al. 2002).

Urinary stones are divided into several groups according to their position within the body and also by the principal components of stones. The main constituents of urinary concretions are phosphate, oxalate and urate (Moroz et al. 2009).

In the past, for the quantitative and qualitative analysis of urinary stone composition mainly solution analysis was utilized, i.e. the stones were dissolved prior this analysis. The biggest disadvantage of this approach is that valuable information on the structure, distribution of individual elements or the composition of the nucleus cannot be obtained. These data are however especially important not only to clarify the beginning and growth of urinary stones, but also to facilitate the healing process.

Using laser ablation based methods, e.g. LA–ICP–MS; it is possible to study the distribution of elements across a variety of important lines in stones (Chaudhri et al. 2007). This method allows us to distinguish between urinary stone structures, as the core or the outer edge. Also, information about the correlation of selected major and trace elements can be obtained from the 2D or 3D maps of these elements.

Here we demonstrate that the LA-ICP-MS in fast line scan mode is sufficiently sensitive for elemental mapping most of important minor and major elements that are present in uroliths. The results obtained by LA-ICP –MS measurements were also compared with results obtained by infrared spectroscopy.

Materials and methods

The investigated samples were urinary stones surgically removed from the patient's body. After the removal the stones were rinse with water and dried. Infrared spectroscopy was performed in order to identify the major components and the type of urinary stone. For subsequent LA–ICP–MS mapping the stones were cut into half. Part of the stone was embedded in epoxy resin, and mapped. All measured samples were from the collections of Professor Petr Martinec, UGN Ostrava.

For LA the UP – 213 ablation system (New Wave Research, USA), equipped with a Nd:YAG laser emitting radiation at a wavelength of 213 nm was used. The created aerosol was introduced using a carrier gas into the inductively coupled plasma with quadrupole mass analyzer and electron photomultiplier detector Agilent 7500ce (Agilent, Japan). The ablation laser was used in line scan mode. The optimized parameters, fixed during the measurements were: integration time 0.01 s, repetition rate 5 Hz, the feed rate (speed of movement) of the sample 40 µm s^{-1}, laser power density 6.56 J cm^{-2} and beam diameter 65 µm. Set of ablation lines was directed across the whole surface of the sample cross section and individual lines were spaced at the distance of 100 µm.

The signals obtained for selected isotopes during ablation of each line scans were then stacked in 2D maps using Grams32 software.

Results and Discussion

As an example, Fig. 1 shows the ^{44}Ca distribution on the cross–section of urinary stone no. 11 727. This sample is oval bladder stones, for which the contents of major components were determined using infrared spectroscopy. This is a whewellite sample, which is covered on the surface with a thin apatite layer.

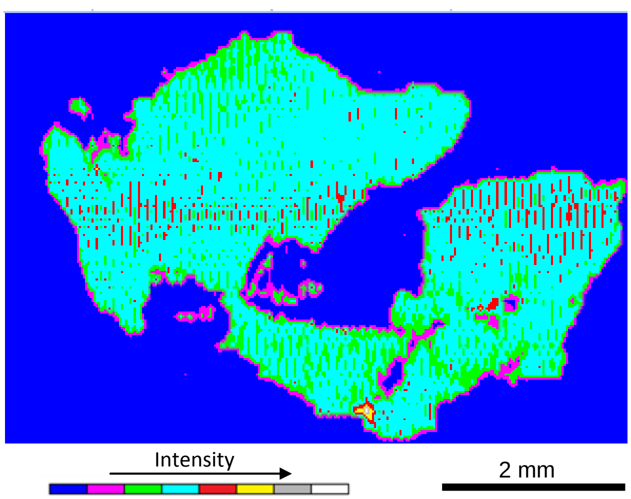

Figure 1: Map of ^{44}Ca

The following isotopes of selected elements were measured: ^{12}C, ^{23}Na, ^{24}Mg, ^{31}P, ^{39}K, ^{43}Ca, ^{44}Ca, ^{55}Mn, ^{56}Fe, ^{63}Cu, ^{66}Zn, ^{109}Ag, ^{118}Sn, ^{208}Pb. Maps were created for all isotopes and it was found that the main ingredient of this stone is ^{44}Ca.

It was also observed, that in several places of the stone cross–section the reduction in ^{44}Ca content is in balance with the increment of ^{12}C. This indicates the presence of calcium oxalate. In some places trace contents of ^{31}P were detected, which may point out the presence of apatite (calcium phosphate).

The texture and the quantitative mineralogical composition of selected calcium oxalate–based urinary stone fragments were also investigated by synchrotron radiation X–ray microtomography.

Conclusion

Maps created by LA–ICP–MS confirmed the results obtained from infrared spectroscopy. The selected urinary stone was whewellite (calcium oxalate) with traces of apatite (calcium phosphate). On the frame of the ongoing work the stone is further investigated. The presence of trace elements and their correlation with matrix elements is studied.

Acknowledgement

We acknowledge the Ministry of Education, Youth and Sports of the Czech Republic for bestowing the research projects OC09013, E08002 and MSM0021622412 and the Czech Grant Agency for the project GA203/09/1394. J.K. Acknowledges Central European Initiative (CEI) for Ceres fellowship.

References

Chaudhri MA, Watling J, Khan FA (2007) Spatial distribution of major and trace elements in bladder and kidney stones. Journal of Radio analytical and Nuclear Chemistry, 271(3):713 – 720

Moroz TN, Palchik NA, Dar'in AV (2009) Microelemental and mineral compositions of pathogenic biomineral concrements: SRXFA, X–ray powder diffraction and vibrational spectroscopy data. Nuclear instruments & methods in physics research section A – Accelerators spectrometers detectors and associated equipment, 603(1-2):141 – 143

Sperrin M, Rogers K, Lane D (2002) An investigation into the architecture and composition of a urinary calculus. Journal of materials science 13(1):7–9