



Strategies for the identification of urinary calculus by laser induced breakdown spectroscopy

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ARTICLE INFO

Article history:

Received 15 January 2009

Received in revised form 23 March 2009

Accepted 27 March 2009

Available online 5 April 2009

Keywords:

Laser induced breakdown spectroscopy

(LIBS)

Urinary calculus

Identification

ABSTRACT

The present work studies two different strategies to identify urinary calculus. On one hand, (linear or parametric and rank or non-parametric) correlation methods using a μ -LIBS system are studied. On the other hand, elemental ratios of reference materials are determined by using a higher-energy laser and an Echelle spectrograph with an ICCD camera, although without microscope. A data-treatment method was applied for each system and real samples of kidney stones – previously analyzed by IR spectroscopy – were used for reliable evaluation of two identification strategies.

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1. Introduction

Stone formation in urinary tracts or kidney is known as urolithiasis. About 4% of Spanish women and men develop a kidney stone at some time in their life—an increasing prevalence in both sexes. Its incidence rate is 0.27% in Spain; therefore, there are 1.7 millions of inhabitants suffering from kidney-stone disease and 100,000 new cases appear every year [1].

Approximately 75% of these stones are usually composed of calcium sales (50% of these stones are calcium oxalate, CaOx) and 10–20% are composed of uric acid (UA). In Zaragoza (Spain), an epidemiology study showed that 40% of stones are composed of calcium oxalate (CaOx), 30.6% of calcium oxalate and calcium phosphate (CaP) mix, 21.7% of uric acid, 0.9% of magnesium ammonium phosphate (MgP), 0.9% of cystine and 5.9% of others (sodium urate, calcium carbonate, etc.)

Therapy to prevent calculi recurrence requires estimating the composition of urinary calculi. Traditional wet chemistry techniques, X-ray diffraction and infrared (IR) spectroscopy are the current analytical methods [2]. These techniques include some disadvantages; for instance, wet chemical analysis requires large sample amounts, while X-ray diffraction cannot detect amorphous samples. IR spectroscopy has been applied within clinical chemistry but often provides complex spectra with contributions from a sizeable number of unknown interfering substances [2]. IR spectroscopy has often been combined with complex software such as

multivariate calibration methods. Thus, Fourier transform infrared spectroscopy (FT-IR) has been used to perform a computerized search in several libraries and partial least-squares (PLS) regression has been tested for the most frequent urinary compositions. However, these techniques require several steps of data preprocessing [3]. To minimize data treatment, artificial neural network models for detecting the most frequent stone compositions have been studied [4] and a single reflection accessory for FT-IR and neural network algorithm interpretation has been developed; however, visual inspection of spectra is still necessary [2].

Laser induced breakdown spectroscopy (LIBS) or Laser induced plasma spectrometry (LIPS) has been used for clinical analysis [5–8]. LIBS' advantages for clinical analysis are: sample treatment is not necessary and little amount of sample is used; this technique is not destructive and, therefore, the sample may be re-analyzed by means of other techniques; and it is very fast and the sample can be studied by using microscope when the μ -LIBS system is used.

LIBS has been used to identify organic compounds by means of different strategies: (i) correlating the LIBS spectrum of unknown compounds with library spectra [9,10], (ii) determining the ratios of different emission lines and molecular bands [11–16], and (iii) using artificial neural networks [17]. The parametric and non-parametric correlation method involves studying multiple emission lines and molecular bands. However, methods working with determining ratios almost exclusively consist of a few lines and bands.

Although limitations for identification exist – due to the loss of molecular information in plasma – the technique achieves excellent potential for online, real-time analysis. Nd:YAG laser has been used for other applications due to its simplicity, easy operation, high efficiency, low cost and suitability. Previous papers [9,10] have

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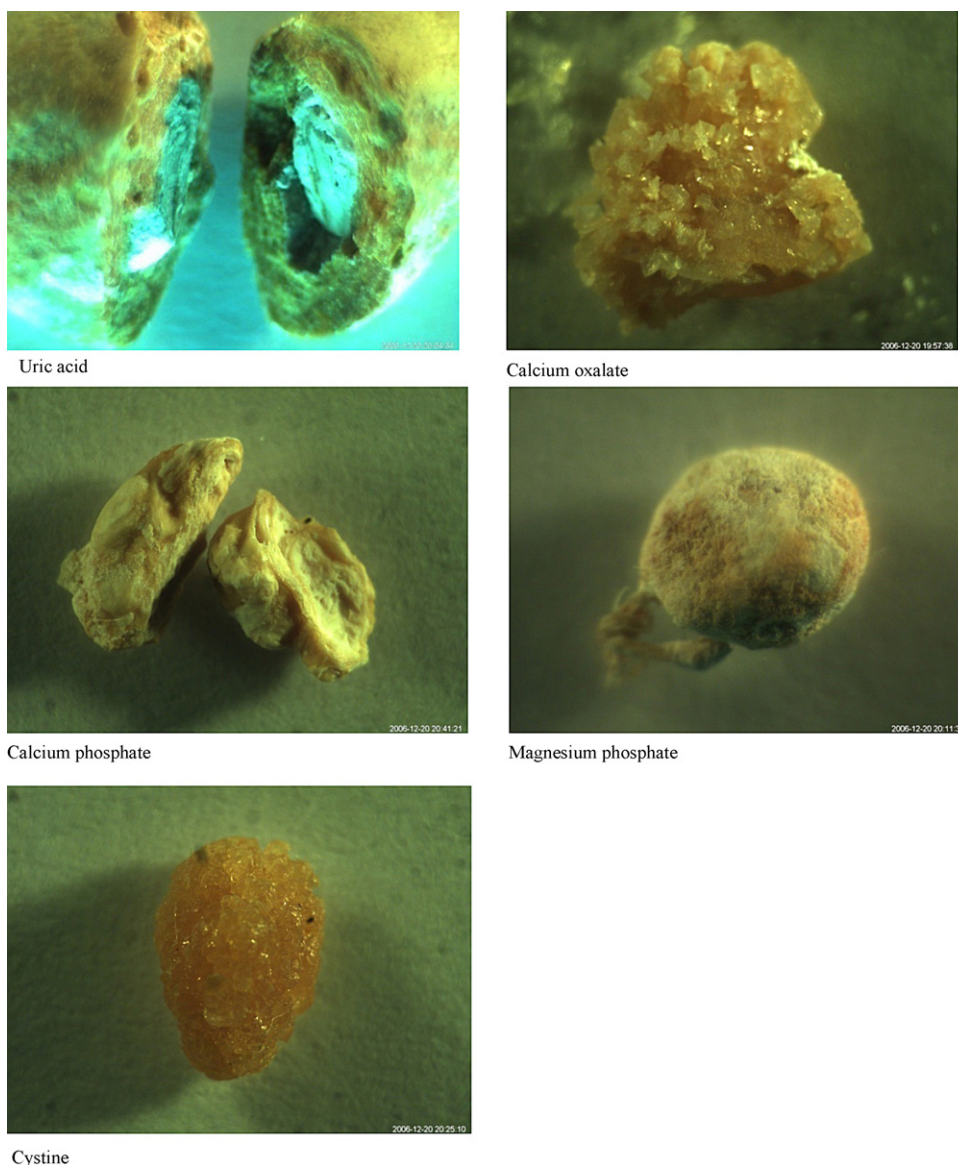


Fig. 1. Kidney stones analyzed.

shown that simple statistical correlation methods – such as linear and rank correlations – can be successfully applied for the identification of solid and particulate materials. Other papers prove the application of the LIBS technique for elemental analysis of renal calculus with concentrations of majority elements both in percentages (Ca and Mg) and ppm (Na, K, Sr, etc.) [19], and for analysis of the spatial distribution of these elements [20] in renal calculus. However, results on the different elements are only at quantitative level and these works do not clearly study the application of LIBS for renal-calculus identification. These papers reveal that LIBS offers a suitable method to obtain quantitative information [19,20] on spatial distribution [20] of elements in the different kinds of stones found in the human body, without destroying the stones.

Two different strategies and instruments are studied in the present work. On one hand, (linear or parametric and rank or non-parametric) correlation methods using a μ -LIBS system are studied. On the other hand, elemental ratios of reference materials are determined by using a higher-energy laser and an Echelle spectrograph with an ICCD camera, although without microscope.

The aim of the first strategy is identifying urinary calculus by means of a μ -LIBS by using a spectrum library, and linear and rank

correlation. This method involves studying all emission lines and molecular bands appearing in spectra from 200 to 850 nm. The objective in the second strategy is to identify kidney stones by determining intensity ratios from elemental lines and measuring ratios of several elements such as C, Ca, H, Mg, N, O and P.

2. Experimental

2.1. Reactives and samples

The library was prepared from the most frequent composition of urinary calculi by using calcium oxalate, calcium phosphate, cystine (Scharlau, extra pure), uric acid (Panreac, PRS) and mixes (calcium phosphate and magnesium phosphate 1:1, calcium oxalate and calcium phosphate 1:1) as reference materials. A pellet of each compound and mix was prepared. Standards (0.50–0.75 g) were mixed with a mortar and pressed at 10^5 N for 5 min.

Real samples of kidney stones provided by the University Hospital of Zaragoza were analyzed. Some samples were broken open to analyze their interior part, since stone core may differ from stone exterior; stone core is the reason for the occurrence of urinary calculus. Photographs of the most frequent stones are shown in Fig. 1.

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