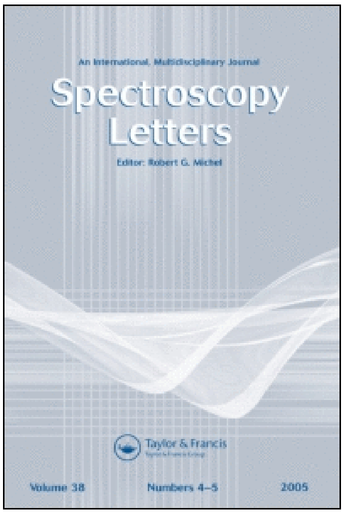

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A VIBRATIONAL SPECTROSCOPY STUDY OF “URINARY SAND”

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Key words: “Urinary sand”, Raman, FT-IR, Voigt profile.

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Abstract

Laser Raman Spectroscopy and FT-IR spectroscopy are used for the study of “urinary sand”. The examination of Raman spectra indicates the presence of struvite and apatite in the sample. The FT-IR spectrum is used to evaluate the relative concentration of apatite/struvite components in the sample. The form of band profile may be correlated to the history of particle growth.

INTRODUCTION

The study of stone formation inside kidney and galley constitutes one of the major problems for the contemporary medicine. Different physical

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techniques like x-ray diffraction, NMR, EPMA, FT-IR and Raman spectroscopy are used to determine the organic and inorganic constituents of "human stones".

The reported results of gallstones' studies show that calcium and phosphorus are the main inorganic elements while the principal organic components are cholesterol, cholic acid, bilirubine, and bilirubine salts[1-4]. Similar studies performed on kidneystones[5-7] report the presence of calcium and phosphorus as major inorganic elements, too. It is important to mention that previous studies of kidneystones by micro Raman spectrometry could not reveal the presence of proteins though their presence in compact zones was observed during their microdissection[6].

Generally, the previous investigations are performed on samples obtained from patients undergoing the elective surgery. The micro spectroscopic techniques are used to get information on small parts of the stone or to control the spatial distribution of one constituent on a polished surface of the stone[1,2,4].

The mechanism of kidney stone formation remains poorly understood though the action of some urea's bacteria or pathologies is suspected as responsible in some cases[6].

We think that the investigation of "urinary sand" provides important information about the process of kidneystone formation. In this paper we present the results of a vibrational spectroscopy study on "urinary sand".

EXPERIMENTAL

SAMPLE. The sample of "urinary sand" was obtained from a patient having a stone in the left kidney. The ultrasonic control reported the presence of many small crystals inside the volume of the right kidney. The sample was collected by filtering his urine on a laboratory filter paper. The "urinary sand" was washed twice with distilled water and dried in open air before measurements.

RAMAN SPECTROSCOPY. Raman spectra were acquired with the micro Raman technique in backscattering geometry. The green line (514.45 nm) of an Ar^+ laser was used as excitation source. The laser power on the sample was approx. 200 mW. The laser beam was tightly focused onto the sample by a microscope objective (Olympus, ULWD80, NA 0.75).The collected Raman light was recorded using two types of spectrometers (Spex double model 1403 monochromator, Dilor XY- triple monochromator) and detectors (nitrogen cooled CCD, optical multichannel array). Spectra are recorded from single microscopic particles with dimensions 5- 20 μm (see Fig.1). However, we could not record spectra on particle agglomeration because of fluorescence. It is necessary to mention that fluorescence hindered the Raman spectrum of some single particles, too.

FT-IR SPECTROSCOPY. FT-IR spectra were recorded applying a BRUKER IFS 120 HR spectrometer. The spectra were obtained from solid, finely grounded sample (KBr).

SPECTRA TREATMENT. We used the software package Spectra Calc for the mathematical treatment of spectra. The identification of molecular compounds in the sample is based on previous research reported in references [6,8].

RESULTS AND DISCUSSION

Raman spectra measured on six particles are presented in Figs. 2 and 3. The spectra in Fig. 2 are excited by approx. 200 mW laser power at the source and are recorded by an optical multichannel array (OMA) of a XY-Dilor spectrometer. The spectra in Fig. 3 are excited by more than 200 mW laser power at the source and are recorded applying the scanning multichannel technique[9] in combination with a CCD camera and a Spex double monochromator.

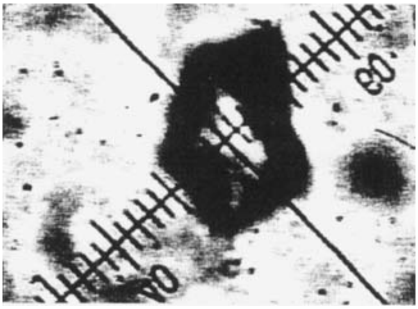

Fig. 1: The view of a single particle (11x6 μm^2) under the microscope.

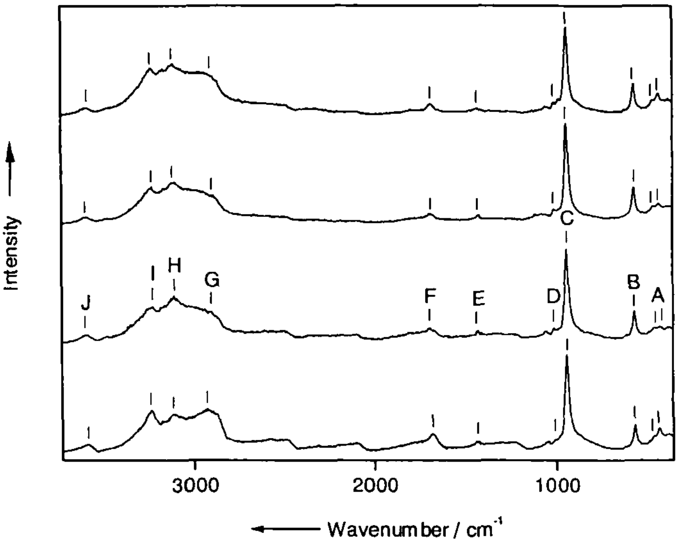

Fig. 2: Raman spectra recorded on four struvite particles.

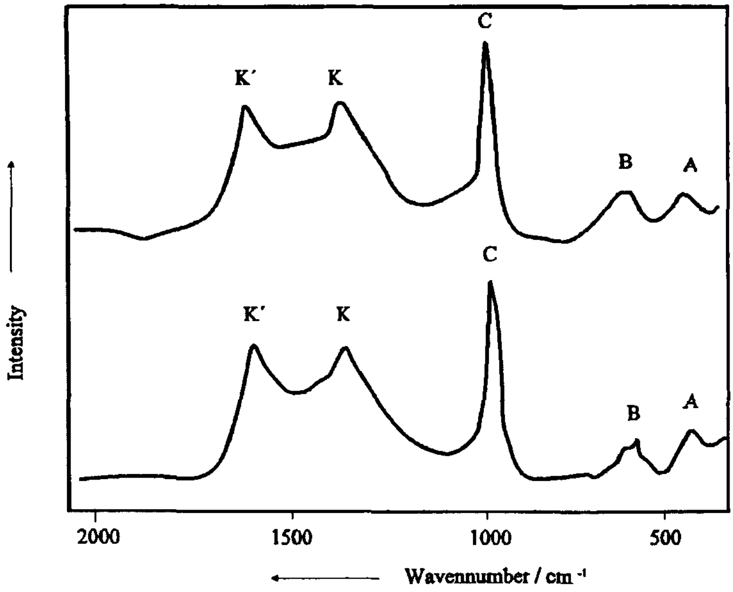

Fig. 3: Raman spectra recorded on two apatite particles.

The most discerned feature, the Raman band labeled by C is positioned at 942 cm^{-1} in the spectra of Fig. 2 and at 960 cm^{-1} in the spectra of Fig. 3. Previous investigations of phosphate ion compounds by vibrational spectroscopy[8] show that the Raman band denoted by C in Figs. 2 and 3 can be related to the A_1 symmetric stretching vibration of $(PO_4)^{3-}$ in struvite (944 cm^{-1}) and apatite (960-964cm^{-1}). The assignment of Raman bands observed on struvite and apatite particles is given in Table 1.

While the spectra in Fig. 2 identify the corresponding particles as struvite compounds ($NH_4Mg(PO_4)*6H_2O$), it is difficult to give precise information about the origin of particles corresponding to the spectra of Fig. 3. Although the position of band C in these spectra suggests the presence of apatite, the position of bands A and B does not constitute a sufficient information to distinguish between different apatite structures, i.e. flour apatite ($Ca_5(PO_4)F$,

Table 1. Assignment of observed Raman bands of Fig. 2 and Fig. 3.

label	Wavenumber Shift in cm^{-1}	Assignment	Ref.
A	430, and 459 (Fig. 2) 435 (Fig. 3)	E bending mode of $(PO_4)^{3-}$ in struvite E bending mode of $(PO_4)^{3-}$ in apatite	8
B	562 (Fig. 2) 600 (Fig. 3)	F_2 antisym. bending mode of $(PO_4)^{3-}$ in struvite F_2 antisym. bending mode of $(PO_4)^{3-}$ in apatite	8
C	944 (Fig. 2) 963 (Fig. 3)	A_1 sym. stretching mode of $(PO_4)^{3-}$ in struvite A_1 sym. stretching mode of $(PO_4)^{3-}$ in apatite	8
D	1012 (Fig. 2)	F_2 antisym. stretching mode of $(PO_4)^{3-}$ in struvite	8
E	1426 (Fig. 2)	F_2 mode of $(NH_4)^+$ in struvite	8
F	1682 (Fig. 2)	E mode of $(NH_4)^+$ in struvite	8
G	2875 (Fig. 2)	–C–H symmetric streching mode of CH_3	10
H	3110 (Fig. 2)	=C–H symmetric streching mode of CH_3	10
I	3237 (Fig. 2)	H_2O vibration in struvite	8
J	3588 (Fig. 2)	OH stretching mode of vibration of OH in struvite	8
K	1350 (Fig. 3)	vibrat. band in low ordered carbon structures	11
K'	1600 (Fig. 3)	vibrat. band in low ordered carbon structures	11

hydroxiapatite $Ca_5(PO_2)_3OH$, etc. The two large bands labeled by K (≈1350 cm^{-1}) and K' (≈1600 cm^{-1}) correspond to the low ordered carbon structures[11], although we can not find any justification for the presence of carbon in "urinary sand". Perhaps it may be related to some carbon impurities on the support or the modifications happening in the sample under the light irradiation. At this point it is important to mention that we could not reveal the presence of calcite, aragonite or other Ca-corresponding structures by Raman spectroscopy.

The FT-IR spectrum of "urinary sand" is presented in Fig. 4. The main features of this spectrum can be identified[8] to struvite and apatite vibrations as given in Table 2.

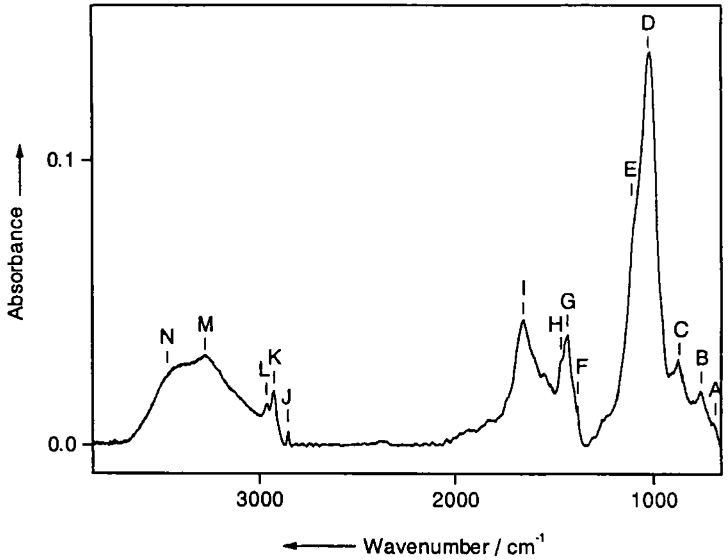

Fig. 4: The FT-IR spectrum of "urinary sand".

Considering reference 10 we related the following bands to organic compounds: F-band (1384 cm^{-1}) to symmetric deformation of CH$_3$, J-band (2852 cm^{-1}) and K-band (2925 cm^{-1}) to CH symmetric and antisymmetric stretching modes of CH$_2$, respectively, L-band (2962 cm^{-1}) to degenerate stretching mode of CH$_3$.

We could not assign some other bands at 1235, 1550, 1823, 2388 cm^{-1}. We think that these bands are due to the presence of other chemical compounds. Thus the FT-IR spectrum reveals the presence of struvite, apatite and organic compounds in "urinary sand". There are no bands corresponding to other Ca-based compounds in this spectrum. We evaluated the relative concentration of apatite/struvite by the areas of spectral bands corresponding to the antisymmetric stretching mode F$_2$ of (PO$_4$)$^{3-}$ in apatite (1092 cm^{-1}) and struvite (1012 cm^{-1}). To achieve this information we decomposed the related

Table 2. Assignment of observed FT-IR bands in Fig. 4.

label	Wavenumber shift in cm^{-1}	Assignment	Ref.
A	695	H_2O libration in struvite	8
B	756	H_2O libration in struvite	8
C	875	H_2O libration in struvite	8
D	1015	F_2 antisym. stretching mode of $(PO_4)^{3-}$ in struvite	8
E	1092	F_2 antisym. stretching mode of $(PO_4)^{3-}$ in apatite	8
F	1384	symmetric deformation of CH_3	10
G	1436	F_2 antisym. bending mode of $(NH_4)^+$ in struvite	10
H	1465	F_2 antisym. bending mode of $(NH_4)^+$ in struvite	10
I	1658	OH bending mode in struvite	8
J	2852	CH symmetric stretching mode of CH_2	10
K	2925	CH antisym. stretching mode of CH_2	10
L	2962	degenerate stretching mode of CH_3	10
M	3274	H_2O vibration mode	8
N	3460	OH stretching mode	8

spectral region into six Voigt bands[a] (see Fig. 5). The main characteristics of fitting bands are presented in Table 3.

According to the area ratio of absorbance bands A and S the relative concentration of apatite/struvite is 0.52. The determination of this parameter is important for medical diagnosis and treatment of the patient. A further interesting result concerns the form of these two bands. It is well known that the Gaussian part of experimental bands can be related to the "impurities" and, in general, to the statistical influences inside the sample. From this point of view one may say that struvite components are grown in "stabilised conditions". This means a determined zone of the kidney and/or missing of

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[a] The baseline is fitted by a linear function.

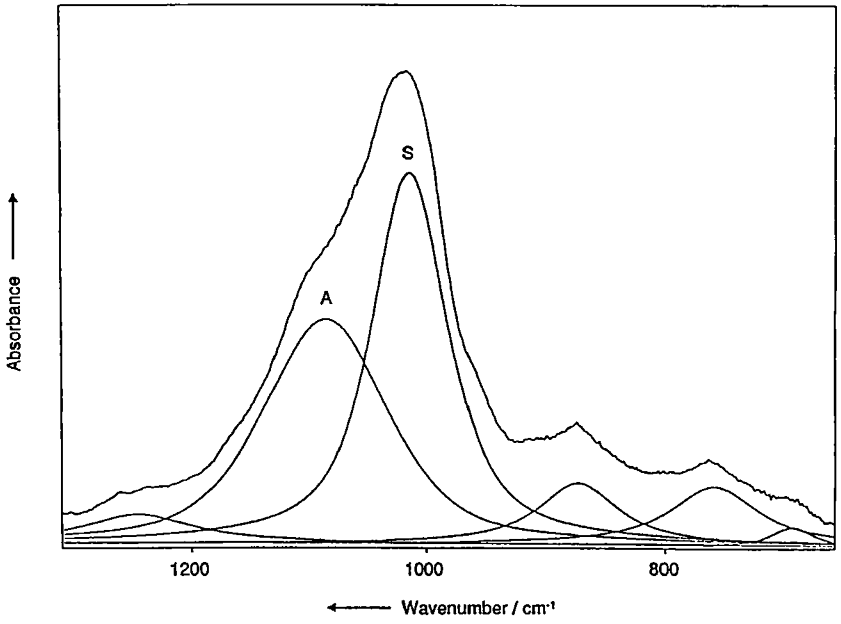

Fig. 5: The spectrum decomposition in the spectral region of interest.

Table 3. The main features of fitting Voigt bands.

Centre of fitting band in cm^{-1}	% of Gaussian part	Area of spectral band
690	43	0.21
758	0	2.56
873	0	3.1
1013 (S-struvite)	8	14.13
1085 (A-apatite)	100	7.64
1235	0	2.84

Table 4. The position and Gaussian percentage of C-bands fitting by Voigt profile.

Spectrum No. /compound	Centre of fitting band in cm^{-1}	% of Gaussian part
1 / struvite (Fig. 2)	942.0	18
2 / struvite (Fig. 2)	941.5	7
3 / struvite (Fig. 2)	942.5	11
4 / struvite (Fig. 2)	942.3	0
1 / apatite (Fig. 3)	959.8	67
2 / apatite (Fig.3)	959.9	66

"impurities" during the growing process. The opposite may be said for the apatite component because its band has practically a Gaussian form. We controlled this hypothesis by the form of band C with Raman spectra corresponding to struvite and apatite particles. The results of their fittings by Voigt profiles are presented in Table 4 and show a higher percentage of Gaussian components to apatite structures, too.

A further useful information of the FT-IR spectrum concerns the presence of organic compounds indicated by bands labeled by K, L, and M. We could not identify them precisely according to the lack of spectral information. We could relate some Raman bands in struvite particles to the organic structures. The missing of related bands in Raman spectra of apatite particles may be explained by the destruction of these structures under the laser irradiation or their presence only in struvite particles. We think that FT-Raman microspectrometry may help to clarify the relative importance of these two factors.

CONCLUSIONS

The results of this study show that vibrational spectroscopy provide important data on the constituents of "urinary sand". The possibilities of vibrational spectroscopy for the evaluation of concentration of the components are very useful for the medical diagnosis and consequently for the prevention of stone growth. The presence of organic compounds on struvite particles of micron dimensions may be very important for understanding the process of stone formation. Additionally, the correlation between band profile and the formation of the sample may open a new and very interesting way for understanding the process of human stone formation.

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