Arabian Journal of Chemistry (2016) 9, 330–334

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

FTIR spectroscopic study of human urinary stones from El Bayadh district (Algeria)

Khaled Sekkoum [a,b], Abdelkrim Cheriti [a,*], Safia Taleb [b], Nasser Belboukhari [a]

[a] Phytochemistry & Organic Synthesis Laboratory, University of Bechar, 08000 Bechar, Algeria
[b] Material & Catalysis Laboratory, D. Liabès University, 22000 Sidi BélAbbès, Algeria

Received 12 July 2010; accepted 10 October 2011
Available online 17 October 2011

KEYWORDS

Urinary stone;
FTIR spectroscopy;
El Bayadh;
Analysis;
Chemical composition

Abstract Identification of components of urinary stones is essential to provide information about the etiological factors considered responsible for stones formation making the therapy and the prevention possible. Morphological examination combined to infrared spectroscopy can provide helpful information about its chemical composition. As the composition of urinary stones varies from one place to another, we have undertaken a study by FTIR of constituents of urinary stones from various patients of El Bayadh region (south west of Algeria).

1. Introduction

Urinary calculi are one of the most painful diseases that life can be afflicted with (Curhan, 2007; Shokouhi et al., 2008). Recent studies in the world concluded that the prevalence of urolithiasis has been increasing for about half a century (Vupputuri et al., 2004; Chandhoke, 2007; Alsheyab et al., 2007). The chemistry of stone is a reflection of what chemical group or moieties are available in the urine at the time of formation and growth of the stone (Carmona et al., 1997). Among the achievements of the last decades is the establishment of methods for the determination of structure and composition of urinary calculi, which is of interest both for the correct identification of the type of stone disease and to provide dues to etiopathogeny (Estepa and Daudon, 1997). Infrared spectroscopy is emerging as a powerful analytical tool, suitable for determining all crystalline, amorphous or poorly crystallized components, mineral and organic molecules and to distinguish between various crystalline phases of a given substance (Kanchana et al., 2009; Bhatt and Paul, 2008; Lu et al., 2000; El khabbaz et al., 2000; Moore, 2007). More than 65 different molecules (including 25 of exogenous origin) have been found in urinary calculi (Fazil Marickar et al., 2009). Extensive analysis of morphology and composition has led to a classification of urinary stones in seven distinctive types and 21 sub-types, including monohydrate (whewellite) and dehydrate (weddellite) calcium oxalates, phosphates, uric acid, urates, protein and cystine (amino acid) calculi. In human urine, the same urinary component can crystallize in different forms. Therefore, the addition of morphological examination to IR stone analysis is very much necessary to identify not only the molecular species present in the stone, but also the crystalline form (Dulce, 1958; Daudon, 2005). In continuation of our urolithiasis study

* Corresponding author.
E-mail address: karimcheriti@yahoo.com (A. Cheriti).

Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2011.10.010

in the south of Algeria (Sekkoum et al., 2008, 2010), the present work report the usefulness of FTIR spectroscopy technique in the study of biochemical composition of stones in the south west of Algeria.

2. Experimental

A total of 62 stones have been collected from El Bayadh city hospital (south west of Algeria), 39 surgically removed and 23 spontaneously expulsed. The samples were washed with distilled water to remove loose debris such as blood, mucous and casts and then air-dried for several days (Bhatt and Paul, 2008). The morphological features and structural characteristics were noted after an examination of each sample by a binocular loupe (Estepa and Daudon, 1997; Nayir, 2002). Then, a transparent pellet of 13 mm has been prepared out of a small amount of fine powder of the calculi material and potassium bromide under pressure using a specially evacuated die. For each stone, four independent samples were prepared-from the core, cross section, and external layer of calculi, and a mixed sample from all parts. To minimize the influence of sample concentration and non-homogenous distribution of sample particles in KBr pellet on linearity of Beer's calibration curve three independent pellets in the concentration range of 0.1–0.5 mg was produced and measured (Carmona et al., 1997; Estepa and Daudon, 1997; Kanchana et al., 2009; Bhatt and Paul, 2008). The FTIR analysis was performed using Nicolet AVATAR 320 FTIR Spectrophotometer by Thermo Electronic Corporation. The spectral region investigated was from 4000 to 400 cm^{-1}. The evaluation menu provided in the Omnic (7.0 version) software performs the entire process automatically. All together, 168 infrared spectra of different parts of urinary calculi were recorded and analyzed.

3. Results and discussion

The results of microscopic examination of the different parts of samples and the main etiologies responsible for stone formation are regrouped in Tables 1 and 2.

Table 1 Morphological type of the external layer.

Type	Male (%)	Female (%)	Total (%)	Main etiologies
Ia, Ib, Ic	36.13	65	50.56	Hyperoxaluria
IIa, IIb, IIc	13.63	30	21.81	Hypercalciuria
IIIa, IIIb, IIIc	8.72	10.22	9.47	Hyperuricosuria

The microscopic examination of the nucleus and peripheral layers of the stone may be very important to identify its morphological type and the metabolic disorder responsible for the stone nucleation or growth process.

The type I which corresponds to a composition in whewellite was dominated in the external layer of the majority of stones especially in the female gender (65%). The power presence of the sub-type Ia in the majority of stones core compared to other types means that hyperoxaluria may be the principal cause of nucleation. Hypercalciuria was the second etiology responsible for the nucleation process in 17.74% case; however, the hyperuricosuria occupied the third place (14.51%).

Figs. 1–6 show some FTIR spectra selected from different parts of urinary stones analyzed. Table 3 represent the principals IR-bands registered and the corresponding stones composition and Table 4 regroup the frequency of the different components recorded in our stones series.

Calcium oxalate is the main component of our urinary stone series. Pure calcium oxalate monohydrate was characterized by five bands between 3486 and 3060 cm^{-1}, due to symmetric and asymmetric O—H stretching, high absorbance at 1618 and 1312 cm^{-1} belonging to C═O and C—O, respectively. Two bands at 782 and 667 cm^{-1} corresponding to C—H bending mode and out of plane O—H bending. An in plane bending of O—C═O arises at 514 cm^{-1} (Fig. 1). The uric acid salt most commonly found in urinary calculi is the anhydrous form; it has a characteristic infrared spectrum easily recognized by the presence of many bands of N—H stretching in the range 3600–2600 cm^{-1}: precisely four high bands appear at 2606, 2678, 2803 and 3016 cm^{-1} corresponding to N—H stretching, and other bands assigned to α and β hydrogen bond (O···H) appearing in 3500–3100 cm^{-1} range. Two characteristic bands; the first centered at 1667 cm^{-1} corresponding to carbonyl (C═O) of urea groups, and the second band at 1588 cm^{-1} attributed to carbonyl of conjugated amid. The C═C stretching appears at 1437 cm^{-1} due to hypsochrom effect of amid and carbonyl groups. The C—N vibrations are located, respectively, at 1115 cm^{-1} of O═C—N and 1028 $cm^{-1}$of ═C—N (Fig. 2). Calcium phosphate or carbapatite was found in a mixture with weddellite; the important spectral characteristics are a large band at 3470 cm^{-1}, which is due to symmetric and asymmetric O—H stretch. The high bands at 1645 and 1323 cm^{-1} correspond respectively to C═O and C—O of calcium oxalate, the phosphine group P═O presents a stretching vibration at 1465 cm^{-1}, a high peak appears at 1028 cm^{-1} can be attributed to P—O of PO_4^{3-} group, and others out of plan deformations (OP═O and O—P—O) of PO_4^{3-} group appears at 776–509 cm^{-1} (Fig. 3). The ammonium urate may be minor

Table 2 Principal causes of nucleation in relation with the gender.

Type	Male (%)	Female (%)	Total (%)	Principal cause of nucleation
Ia	30.87	30.43	30.65	Hyperoxaluria
IIa	25.5	9.98	17.74	Hypercalciuria
IIIa	22.5	6.52	14.51	Hyperuricosuria
IVa	6.44	00	3.22	Hyperphosphaturia + urinary infection
IIb	6.3	13.04	9.67	Hypercalciuria + hyperoxaluria
IIIb	00	9.67	4.84	Hyperuricosuria
Ic	6.57	12.77	9.67	Primary hyperoxaluria
IIIc	6.43	00	3.22	Hyperuricosuria
IIId	00	12.91	6.45	Urinary infection by aminogene bacteria

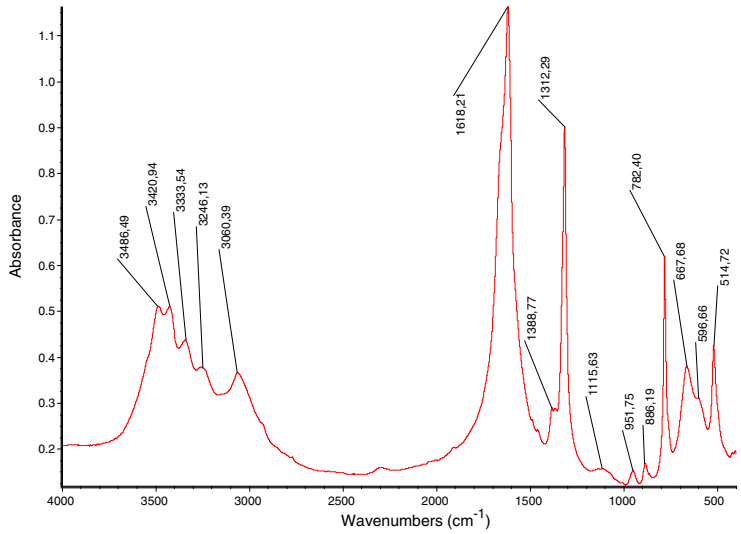

Figure 1 FTIR spectrum of urinary stone core containing pure whewellite.

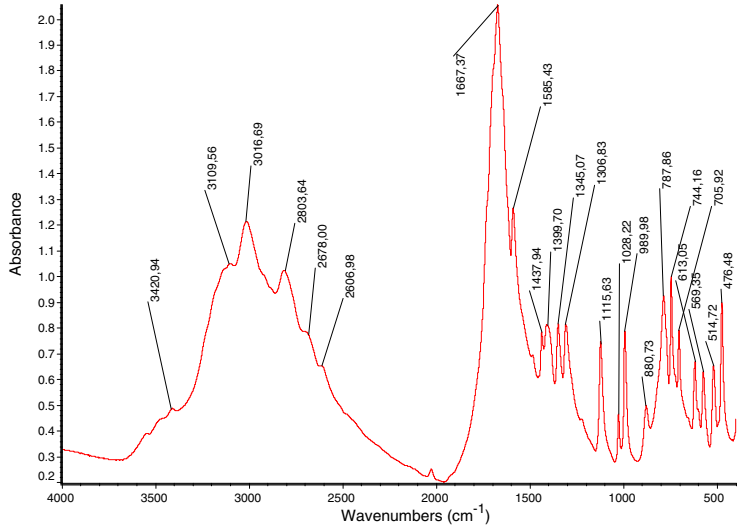

Figure 2 FTIR spectrum of urinary stone core containing pure uric acid anhydrous.

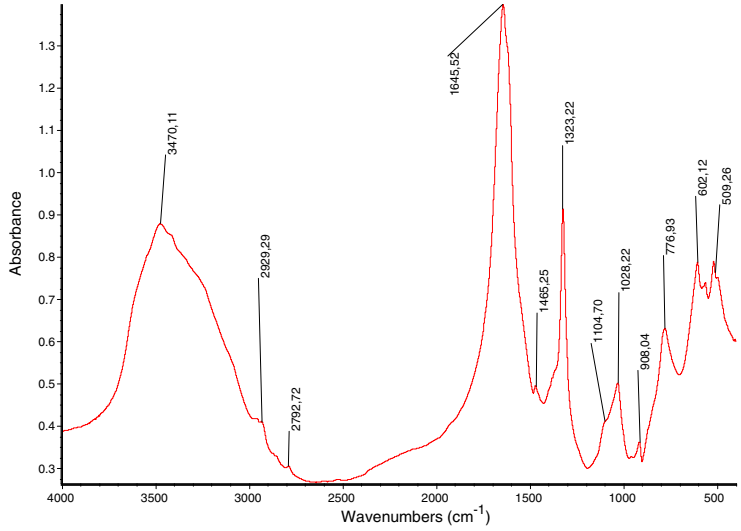

Figure 3 FTIR spectrum of urinary stone cross-core containing weddellite + carbapatite.

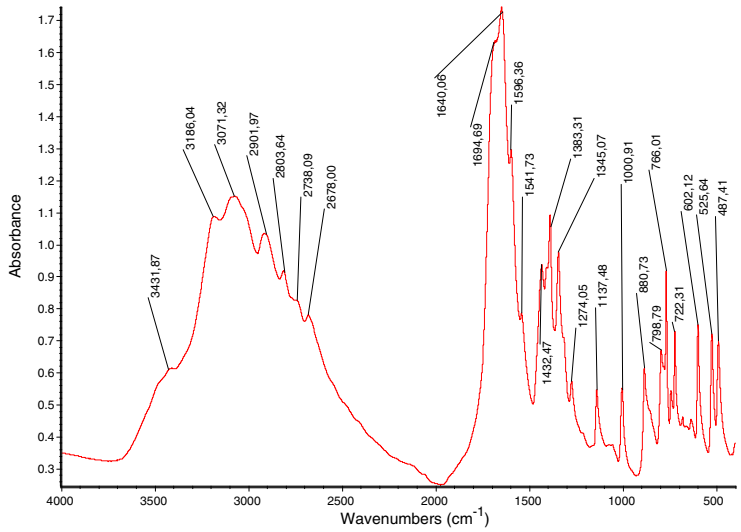

Figure 4 FTIR spectrum of urinary stone cross-section containing ammonium acid urate + whewellite.

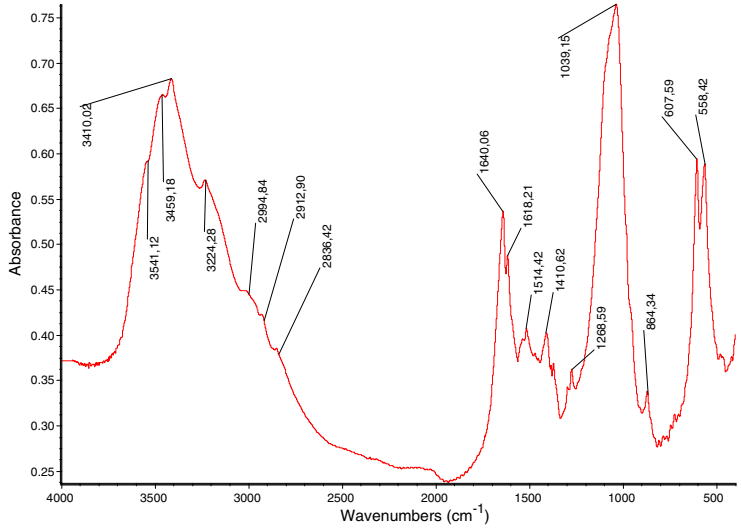

Figure 5 FTIR spectrum of urinary stone section containing weddellite + carbapatite + whewellite + protein.

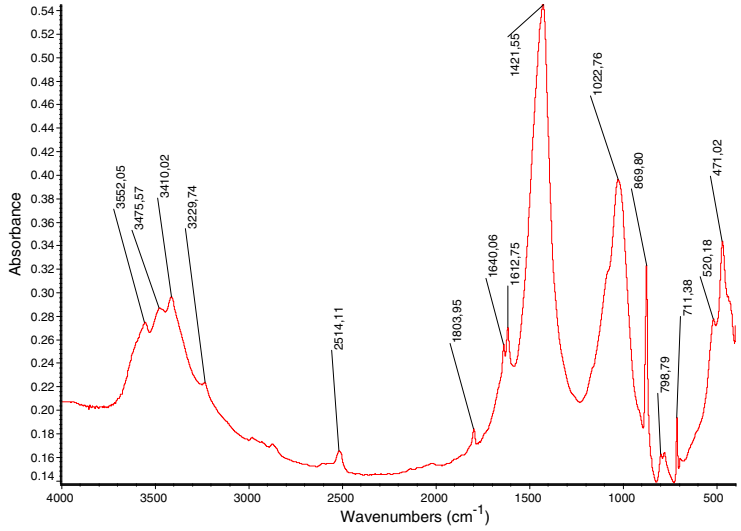

Figure 6 FTIR spectrum of urinary stone section containing calcite + whewellite.

Table 3 Principal IR-bands observed in different FTIR spectra of the main composition of stones.

Main composition	Principal IR-bands observed (cm^{-1})
Whewellite	3486, 3420, 3333, 3060, 1618, 1312, 886, 782, 667, 514
Uric acid anhydrous	3420, 3109, 3016, 2803, 1667, 1588, 1437, 1022, 990, 787, 744, 706
Weddellite + carbapatite	3470, 1645, 1323, 1465, 1028, 602, 560
Ammonium urate acid + whewellite	3431, 3071, 1640, 1345, 1137, 1000, 766, 722, 602
Weddellite + carbapatite + whewellite + protein	3460, 3410, 2912, 1640, 1618, 1410, 1039, 864, 607, 558
Calcite + whewellite + weddellite	3475, 2514, 1804, 1640, 1612, 1421, 870, 711, 520

Table 4 Frequency of constituents identified in urinary stones ($n = 62$).

Constituent	Frequency (%)
Calcium oxalates	58.06
Calcium phosphates	25.81
Purines	12.91
Others compounds	03.22

constituent in urinary calculi (Lonsdale and Mason, 1966), the main infrared characteristic bands (Fig. 4) are found in (3431–2606 cm^{-1}), corresponding to N—H stretching of heterocyclic and ammonium group, high intense absorption of oxime C=N at 1694 cm^{-1} and carbonyl (C=O) of urea groups at 1640 cm^{-1}. A band at 1593 cm^{-1} corresponding to conjugated carbonyl, and valence stretching of =C—O at 1541 cm^{-1}, three bands at 1432, 1383 and 1346 cm^{-1} corresponding to N—H deformation. Stretching vibration of O=C—H appearing at 1274 cm^{-1}. The other vibrations between 1137 and 1000 cm^{-1} are attributed to C—N stretching mode. The two calcium oxalates frequently appearing in urinary calculi are calcium oxalate monohydrate (whewellite) and dehydrate (weddellite). When one of them is in excess in the same mixture, the identification of the minor component may be difficult. Careful examination of the 3600–3000, 1400–1300 and 800–400 cm^{-1} infrared regions makes the difference (Fig. 5). The discrete formation of two bands in the region of 780 and 515 cm^{-1} is very important to distinguish whewellite from weddellite (Cariati et al., 2000). Calcite is rarely found in urinary stones (Joekes et al., 1973); its presence was identified by three bands at 1421, 870 and 711 cm^{-1} correspond, respectively, to asymmetrical stretch, out of plan bending and in plan bending of carbonyl of carbonate ion (Fig. 6). The monohydrate calcium oxalate stone formation is mainly due to primary hyperoxaluria. In contrast, the dihydrated form is due to renal hypercalciuria (Maschio et al., 1981). Ammonium urate is frequently found in human urinary calculi accompanied by calcium oxalate monohydrate (Carmona et al., 1997), generally, it results from high hyperuricosuria.

4. Conclusion

During the last years, the prevalence of urinary lithiasis has dramatically increased in both industrialized and developing countries.

Microscopic examination of the nucleus and peripheral layers of the urinary stones collected from El Bayadh region indicates that type I which corresponds to a composition in whewellite was dominated in the external layer of the majority of stones especially in the female gender (65%). The presence of the sub-type Ia in the majority of stones core compared to other types means that hyperoxaluria may be the principal cause of nucleation (30.65%) followed by hypercalciuria (17.74%) and hyperuricosuria (14.51%). The FTIR analysis of selected different parts of urinary stones confirms these results, that calcium oxalate monohydrate (whewellite) and dehydrates (weddellite) is the main component of our urinary stone series.

The information on chemical composition of urinary lithiasis is a very important step in the therapy of this disease, it is essential for knowing their etiology and in fact making proper management and prevention of its recurrence is possible.

References

Alsheyab, F., Banihani, I., Mosameh, Y., 2007. J. Biol. Sci. 7 (7), 1290–1292.
Bhatt, P.A., Paul, P., 2008. J. Chem. Sci. 120 (2), 267–273.
Cariati, F., Rampazzi, L., Toniolo, L., Pozzi, A., 2000. Stud. Conserv. 3, 180–188.
Carmona, P., Bellanato, J., Escolar, E., 1997. Biospectroscopy 3, 331–344.
Chandhoke, S.P., 2007. Urol. Clin. N. Am. 34, 315–322.
Curhan, G.C., 2007. Urol. Clin. N. Am. 34, 287–293.
Daudon, M., 2005. Ann. Urol. 39, 209–231.
Dulce, H.J., 1958. Urol. Int. 7, 137–139.
El Khabbaz, S., Meiouet, F., El Amrani, A., 2000. Biol. Santé 1 (1), 14–23.
Estepa, L., Daudon, M., 1997. Biospectroscopy 3, 347–369.
Fazil Marickar, Y.M., Lekshmi, P.R., Varma, L., Koshy, P., 2009. Urol. Res. 37 (5), 271–276.
Joekes, A.M., Rose, G.M., Sutore, D.J., 1973. Brit. Med. J. 1, 146–153.
Kanchana, G., Sundaramoothi, P., Jeyanthi, G.P., 2009. JMMS 8 (2), 161–170.
Lonsdale, K., Mason, P., 1966. Science, 1511–1518.
Lu, C.H., Lu, H.F., Chen, W.C., Lee, T., Wu, H.C., 2000. Mid Taiwan J. Med. 5 (2), 73–78.
Maschio, G., Tessitor, N.D., Angelo, A., 1981. Am. J. Med. 71, 623–637.
Moore, A., 2007. Vet. Focus 17 (1), 22–27.
Nayir, A., 2002. Pediat. Nephrol. 17, 425–432.
Sekkoum, K., Cheriti, A., Taleb, S., 2008. Ann. Univ. Bechar 4, 27–37.
Sekkoum, K., Cheriti, A., Taleb, S., Belboukhari, N., Djellouli, H.M., 2010. Asian J. Chem. 22 (4), 2891–2897.
Shokouhi, B., Gasemi, K., Norizadeh, E., 2008. Res. J. Biol. Sci. (6), 620–626.
Vupputuri, S., Soucie, J.M., Mc Clellan, W., Sandler, D.P., 2004. Ann. Epidemiol. 14 (3), 222–228.