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Structural characterization and vibrational studies of human urinary stones from Istanbul, Turkey

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ABSTRACT

Seven human urinary stones were collected from urinary bladders of patients hailing from Istanbul, Turkey. Their XRD, EDX, FT-IR and FT-Raman spectra as well as SEM images have been recorded to determine their chemical compositions, morphologies, crystal structures, and crystallite sizes. XRD and vibrational (FT-IR and FT-Raman) analyses indicate that six out of the seven stones have identical contents. The ratios of organic and inorganic contents of the stones have been determined by their thermogravimetric analyses. The stones have been found to contain calcium oxalate monohydrate and apatite as the major components.

1. Introduction

Urolithiasis is a common urological sickness. It appears between 1%–20% of the general population [1,2]. The frequency of its occurrence is increasing with each passing day [3]. This disease arises from the stone formation in the urinary system, known as kidney (renal) stones, urinary calculus, or calculi. The stone formation mechanism is not fully known. Therefore, analyses on the stone structures are very crucial for proper diagnosis and treatment [4–7]. The structures and compositions of the renal stones are in general complicated since they depend on many factors such as the living environment, diet, age, sex, and metabolism [8,9]. The components of the stones include both crystalline and organic materials at several ratios [10]. Such as, calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$), calcium oxalate dehydrate ($CaC_2O_4 \cdot 2H_2O$), calcium phosphate known also as apatite {$Ca_{10}(PO_4,CO_3)_6(OH,CO_3)$}, calcium hydrogen phosphate dehydrate known also as brushite ($CaHPO_4 \cdot 2H_2O$), magnesium ammonium phosphate hexahydrate knows as struvite ($MgNH_4 PO_4 \cdot H_2O$) and uric acid ($C_5H_4N_4O_3$) [11]. Renal stones containing at least 82 components have been discovered but, only seven components have occurrence higher than 1% [11,12]. The 34% of renal stones includes monominerals while the 44% of the stones grows up with two minerals [13]. The renal stones can be formed into various morphologies. The majority of stones examined are smooth and ovular but some stones may have sharp structures. Drug metabolites affect the nucleation of renal calculi [14].

The presence of renal stones can cause severe pain and sometimes damage the kidneys [15]. To classify the diseases due to renal stones and treat them reliably and efficiently the chemical compositions of the stones needs to be known. A large number of methods are used for analyzing the composition of the renal stone. In recent years XRD and IR spectral measurements have become more popular than the others since they are fast, sensitive, and provide accurate information about the major chemical components of the stone without any destruction [16]. In this study, we perform the structural and morphological characterizations of seven human urinary stones from Istanbul by using X-ray diffraction (XRD), Fourier transform (FT)-IR, FT-Raman, scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and thermogravimetric analysis (TGA).

2. Experimental details

The human urinary stones collected from Istanbul, Turkey, were washed with deionized water to clean debris like mucous and blood. Samples were mixed ground in a mortar to obtain fine powdered samples.

The crystalline structures of the urinary stones were determined by recording XRD spectra with a Rigaku D/Max-IIIC spectrometer using Cu K_α radiation in the 2θ in range of 20°–70°.

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The mid region (4000–400 cm^{-1}) room temperature FT-IR spectra were recorded on Bruker Alpha Series Spectrometer with attenuated total reflectance (ATR) technique by placing the fine powdered renal stones directly into the sample holder without any other process. The room temperature FT-Raman spectra of the fine powdered stones were recorded on a Thermo Nicolet 6700 spectrometer in the mid-IR region using 1024 nm laser as the excitation line. The morphologies of the stones were imagined by SEM on a JEOL JSM 7001F scanning electron microscope. The elemental compositions of stones were identified by SEM–EDX. Thermogravimetric characteristics were measured with a Perkin Elmer STA 6000 analyzer by heating the powdered samples from 30 °C to 750 °C at a heating rate of 10 °C/min under N_2 atmosphere.

3. Results and discussion

3.1. XRD Analysis

Powder XRD patterns of the samples A1–A7 are given in Fig. 1. XRD phase analyses identify the composition of the samples as given in Table 1. The samples A3–A7 have the same composition, i.e., calcium oxalate monohydrate ($Ca_2C_4O_{10}H_{2.57}$, COM). While the sample A1 has apatite composition ($Ca_5P_3O_{13}H_{1.3}C_{0.1}$), the sample A2 is a mixture of COM and apatite. The powder XRD pattern of A2 revealed that the prominent peak (intensity ~80%) is due to COM, with minor peaks due to apatite. These XRD results are also consistent with the present FT-IR and EDX analyses. The thickness t of the samples (average crystallite sizes) was calculated (Table 1) from the line-width of the most intense peak in powder XRD spectra using Scherrer's relation:

$$t = 0.9\,\lambda/(\beta\cos\theta)$$

Table 1
Calculated crystal sizes and compositions card numbers of the samples A1–A7.

Sample	D (nm)	Comp.	Formula	ICDD No
A1	10.87	Apatite	$Ca_5P_3O_{13}H_{1.3}C_{0.1}$	#99-100-3635
A2	44.17	Whewellite	$Ca_2C_4O_{10}H_{2.57}$	#99-100-0774
	13.07	Apatite	$Ca_5P_3O_{13}H_{1.3}C_{0.1}$	#99-100-3635
A3	52.00	Whewellite	$Ca_2C_4O_{10}H_{2.57}$	#99-100-0774
A4	37.37	Whewellite	$Ca_2C_4O_{10}H_{2.57}$	#99-100-0774
A5	53.03	Whewellite	$Ca_2C_4O_{10}H_{2.57}$	#99-100-0774
A6	59.12	Whewellite	$Ca_2C_4O_{10}H_{2.57}$	#99-100-0774
A7	43.77	Whewellite	$Ca_2C_4O_{10}H_{2.57}$	#99-100-0774

where β is the full width at the half maximum (FWHM), λ is the wavelength of the X-ray radiation, and θ is the angle for the most intense XRD peak.

3.2. FT-IR and FT-Raman analyses

The FT-IR and FT-Raman spectra of the samples A1–A7 are given in Figs. 2 and 3, respectively, while the assignments of the vibrational bands are given in Tables 2 and 3.

The IR band at 511 cm^{-1} is due to O–C–O in-plane bending vibration of COM [21]. The bending and stretching vibrations of the PO_4^{-3} ion are known in the region of 300–600 cm^{-1} and 900–1200 cm^{-1}, respectively [17,19]. In this study PO_4^{-3} bendings of apatite appear at 555, 563 and 601 cm^{-1}. The weak band of calcium phosphate crystals at 871 cm^{-1} and it belongs to the CO_3 ion, consistent with literature [18]. The peaks at around 665 cm^{-1} and 779 cm^{-1} are known to arise from the O–H out-of-plane bending and C–C stretching, respectively [20]. These peaks are at 657 cm^{-1} and 778 cm^{-1} in the present study. The C–C stretching of COM is at the 885 cm^{-1} [21]. The C–O stretching is at 953 cm^{-1} and 945 cm^{-1} as weak bands [22,23]. The C–O stretching appears in this study at 949 cm^{-1}. The weak shoulder
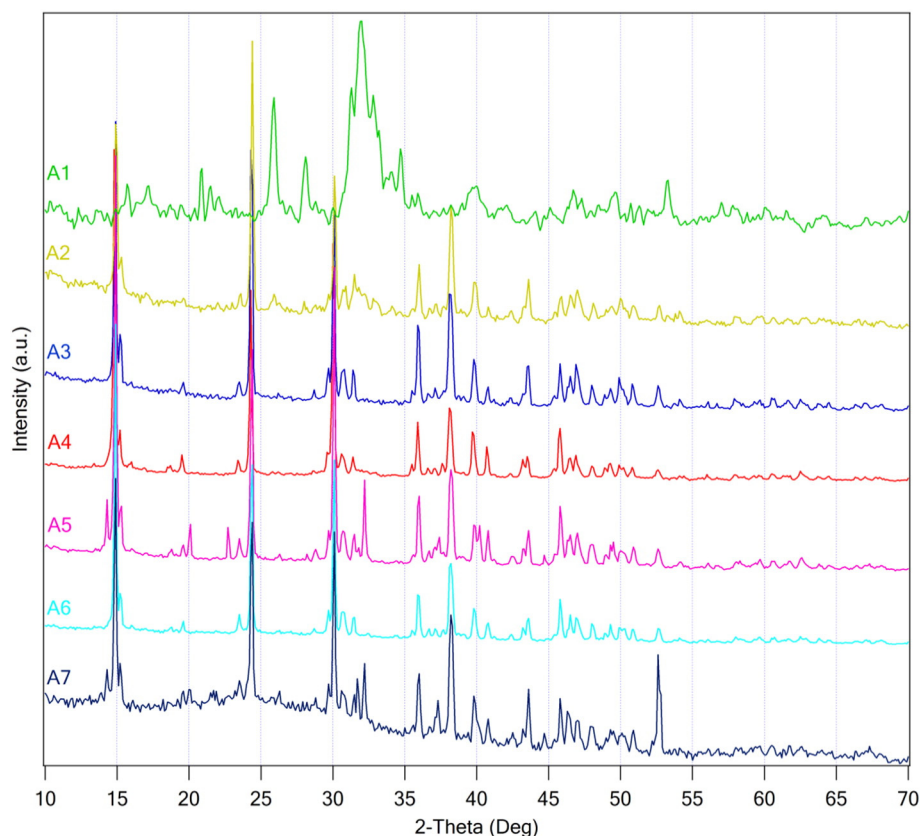

Fig. 1. XRD powder diffraction patterns of the samples A1–A7.