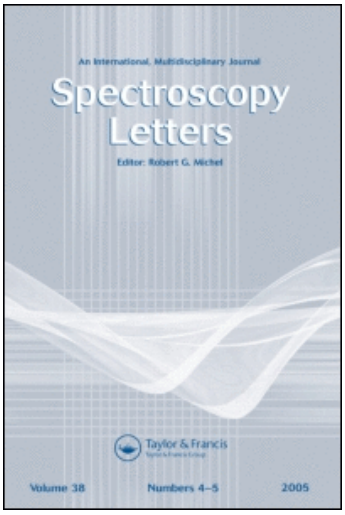

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Online publication date: 25 October 2004

To cite this Article Ouyang, Jian-Ming(2004) 'Identification of Urinary Stone Components by X-Ray Photoelectron Spectroscopy', Spectroscopy Letters, 37: 6, 633 — 641
To link to this Article: DOI: 10.1081/SL-200038685
URL: http://dx.doi.org/10.1081/SL-200038685

SPECTROSCOPY LETTERS
Vol. 37, No. 6, pp. 633–641, 2004

Identification of Urinary Stone Components by X-Ray Photoelectron Spectroscopy

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ABSTRACT

X-ray photoelectron spectroscopy (XPS) has been used for the first time to study the composition of calcium oxalate (CaOxa) stones and uric acid stones. This technique allows for the identification and location of various inorganic and organic species at the same time. In CaOxa stones, there were less than 10% of phosphates. Sectional analyses of these stones indicated that the content of phosphorus in the stone center is higher than that in stone crust. In uric acid stones, CaOxa was rarely found. XPS is able to detect differences in chemical functionality. In uric acid stones, the binding energy (E_b) for nitrogen atoms were about 399.5 ± 0.2 eV, which are largely characteristic of organic nitrogens

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DOI: 10.1081/SL-200038685 0038-7010 (Print); 1532-2289 (Online)

N (−3). In comparison, the E_b values of N (+5) in inorganic compounds are about 401 eV.

Key Words: Urinary stone; X-ray photoelectron spectroscopy; Uric acid; Oxalates.

INTRODUCTION

Urolithiasis constitutes a serious health problem that affects a significant section of mankind occupying between 3% and 14% of the population, depending on the geographical region.[1] For example, the incidence of urolithiasis in white American men and women was 10% and 5%, respectively.[2,3]

The determination of the composition of urinary calculi is important both for the possible prophylaxis of further urolithiasis and for the treatment of the disease. Various methods have been employed to analyze stone composition and morphology. These include chemical analyses (qualitative and quantitative analyses, colorimetry),[4] optical microscopy,[5] Fourier transform-infrared (FT-IR) spectrophotometry,[6,7] thermal analysis (TGA/DTA),[8] powder x-ray diffraction (XRD),[5,9,10] scanning electronic microscopy (SEM),[11] transmission electronic microscopy (TEM),[12] etc. Some advanced techniques such as proton induced x-ray emission (PIXE),[5] Raman spectroscopy,[9,13] and atomic force microscopy (AFM)[14] have also been used to analyze urinary calculi. However, it is difficult to detect a small amount, for example less than 5%, of one composition in a sample by some techniques such as XRD, FT-IR, and TGA/DTA.

X-ray photoelectron spectroscopy (XPS) has been used for numerous applications such as biological surface, catalysis, corrosion, lubrication, electrodes, electronic devices, magnetic storage media, polymers, and interfacial coordination.[15,16] Unlike those techniques mentioned earlier, XPS analyzes the uppermost layers of a solid, including a probed depth of ca. 1.0–10.0 nm depending on the property of the materials probed. This technique can be used for a quantitative analysis of major, minor, and trace elements of very small samples in a single measurement. Much information has been obtained by XPS to help understand the atomic environment of solids at or near the surface.

However, to the author's knowledge, there is no report of the investigation of urinary stones using XPS. The purposes of this work are to identify and locate various inorganic and organic species in urinary stones, to provide information about the mechanism of stone formation, and to estimate the most dominant crystalline structure by studying element ratios by XPS.

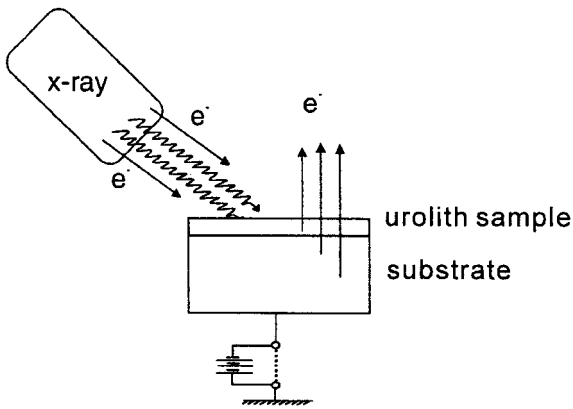
EXPERIMENTAL

Clinical Information

Ten urinary stones were collected between October and December 2001. All the patients were from Guangdong province, which is the region with the highest incidence of urinary stone in southern China. The ages of patients were from 16 to 70 years with an average age of 48.3 years. The male to female ratio was 8 : 2.

Method

Each urolith was washed with distilled water and then vacuum dried. Subsequently, the uroliths were ground to a fine powder in an agate mortar and analyzed using XPS. To assess the compositional variation of uroliths in their centers and in their crusts, a sectional analysis was used for some uroliths. The XPS was performed using an ESCA Lab MKII (VG scientific) photoelectron spectrometer, with a monochromatic Al Kα x-ray radiation source (1486.6 eV) under a vacuum of 10^{-7} Pa. A schematic diagram of the experimental setup is shown in Sch. 1.[17] A two-step procedure[18] was used in these studies. At first, wide scanning spectra of the uroliths were recorded. Inspection of the spectra allows assignment of the observed peaks to particular components. The wide scans were conducted from 0 to 1200 eV with a pass energy of 100 eV. In the second step, the elements,



Scheme 1. Schematic diagram of the experimental setup of XPS. The electrons originating from the x-ray tube represent the low-energy stray electrons.[17]

Ca, C, N, P, and O, were scanned over the energy range of 344–354, 282–294, 395–402, 130–137, and 528–540 eV, respectively, with a pass energy of 20 eV. The charging shift was corrected with the C1s line emitted from neutral hydrocarbon. The XPS data were transformed into values of atom%, which is in proportion to the normalized area and is in inverse proportion to the Wagner factor[15,16,19] as shown in Eq. (1),

$$\frac{Y_1}{Y_2} = \frac{I_1 \times S_2}{I_2 \times S_1} \tag{1}$$

where Y_1/Y_2 is the atomic ratio, I_i is the peak area of ith element, and S_i is the Wagner factor. The Wagner factors of C1s, Ca2p, P2p, N1s, and O1s are 0.31, 1.88, 0.51, 0.49, and 0.72, respectively.

RESULTS AND DISCUSSION

CaOxa Stone

Seven CaOxa stones (S1–S7) and three uric acid stones (S8–S10) were analyzed using XPS. One of the representative XPS survey scans of CaOxa stones is shown in Fig. 1(a). It is marked by the presence of the corresponding Ca2p [Fig. 1(b)], C1s [Fig. 1(c)], and O1s core level peaks. The binding energies (E_b) of various elements in the stones are listed in Table 1. The E_b values of Ca2p and O1s were 347.1–347.8 and 530.1–530.8 eV, which are typical binding energies for Ca (+2) and O (−2) in inorganic compounds.[20–22]

XPS, with its high sensitivity, can detect small amounts of the composition, especially for low Z elements. The values of atom% in uroliths measured by XPS spectra were listed in Table 2. It is in proportion to the normalized area and is in inverse proportion to the Wagner factor,[15,16,19] as shown in Eq. (1) mentioned in Method section.

It can be seen from Table 2 that the average elemental Ca/C ratios of the uroliths S1–S7 approximate 1 : 2, which is in agreement with the stoichiometry of Ca/C of CaOxa (CaC_2O_4).

For the samples S1–S3, no other elements were revealed by XPS. It showed that CaOxa was the dominant phase in these three uroliths. However, in the XPS spectra of the samples S4–S7, in addition to the presence of the corresponding Ca2p, C1s, and O1s core level peaks, a new characteristic peak, although sometimes is very weak, was observed with a binding energy of about 133.4 eV (Table 1), which was assigned to P2p [Fig. 1(d)]. This indicated that there are some phosphates in these four uroliths. As follows from the approximate ratio between areas in XPS spectra of uroliths S4–S7,

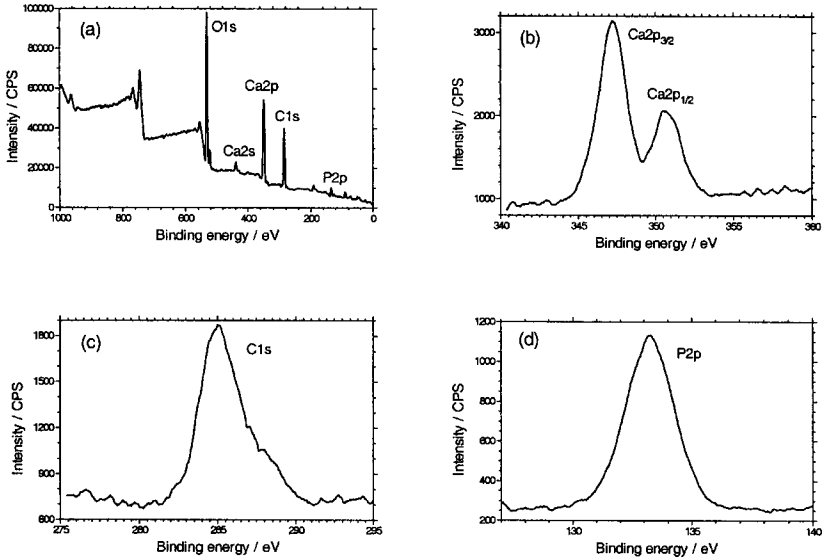


Figure 1. XPS survey scan for (a) CaOxa stone S4, and the narrow scans of (b) Ca2p, (c) C1s, and (d) P2p.

the relative amount of phosphorus did not exceed 10% of the total amount of carbon species. Sectional analyses of these stones indicated that the content of phosphorus in the stone centers is higher than that in stone crusts.

For the four CaOxa stones (S4–S7) containing phosphates, the Ca/C ratios were slightly larger than 1 : 2 (Table 2). It is demonstrated that

Table 1. Binding energies for 2p electrons of calcium and phosphorus and 1s electrons of carbon, oxygen, and nitrogen in uroliths [E_b (eV)].

Samples	Types of urolith	C1s	Ca2p	O1s	P2p	N1s
S1	CaOxa calculus	285.0	347.5	530.6		
S2	CaOxa calculus	285.0	347.4	530.1		
S3	CaOxa calculus	285.0	347.4	530.8		
S4	CaOxa calculus	285.0	347.2	530.7	133.5	
S5	CaOxa calculus	285.0	347.7	530.5	133.2	
S6	CaOxa calculus	285.0	347.1	530.4	133.6	
S7	CaOxa calculus	285.0	347.8	530.7	133.3	400.8
S8	Uric acid calculus	285.0		531.5		399.4
S9	Uric acid calculus	285.0		531.6		399.7
S10	Uric acid calculus	285.0	347.6	531.9		399.6

Table 2. Summary of relative atomic ratios in uroliths measured by XPS.

Samples	Ca	C	N	P	O
S1	1.00	1.98	0	0	4.92
S2	1.00	2.03	0	0	5.21
S3	1.00	2.11	0	0	5.65
S4	1.00	1.87	0	0.09	5.14
S5	1.00	1.89	0	0.06	4.77
S6	1.00	1.92	0	0.06	5.31
S7	1.00	1.98	0.03	0.04	5.21
S8		5.00	3.95	0	3.77
S9		5.00	4.20	0	4.30
S10	0.21	5.00	4.45	0	3.52

most of the phosphates are calcium phosphates, such as hydroxyapatite $\{Ca_{10}(PO_4)_6(OH)_2\}$, octacalcium phosphate $\{Ca_8H_2(PO_4)_6(H_2O)\}$, etc. Because the existence of calcium phosphates in CaOxa stones make the amount of calcium increased, but the amount of oxalate unchanged. Therefore, the Ca/C ratios increased.

Uric Acid Stone

In the XPS spectra of uroliths S8–S10, the core level peaks of C1s, O1s, and N1s (Fig. 2) were dominant. The information on stoichiometry, which is derived from the areas of corresponding elements in XPS spectra, gave the elemental C/N ratios of all the three uroliths to be nearly 5 : 4 (Table 2), with an acceptable deviation. It is consistent with the theoretical C/N ratio of 5 : 4 of uric acid (Sch. 2). Therefore, the three samples (S8–S10) were uric acid stones. For the sample S10, a little calcium was observed. The Ca/C ratio derived from the areas of peaks of Ca and C elements in XPS spectra was 0.21. It indicated that some calcium salts were included in this urolith.

The binding energy in XPS spectra depends on a small but measurable chemical shift due to the atomic charges localized both on the ionized and on the neighboring atoms, and is therefore related to net atomic charges. Although the factors that affect the measured XPS binding energy depend on the nature of the chemical surroundings, a direct experimental characterization of such important quantities as the energy of molecular orbital levels and atomic charge distributions within the coordination sphere are available.

Values of E_b for nitrogen atoms in uroliths S8–S10 were about 399.5 ± 0.2 eV. According to reference data on E_b for N1s core electrons

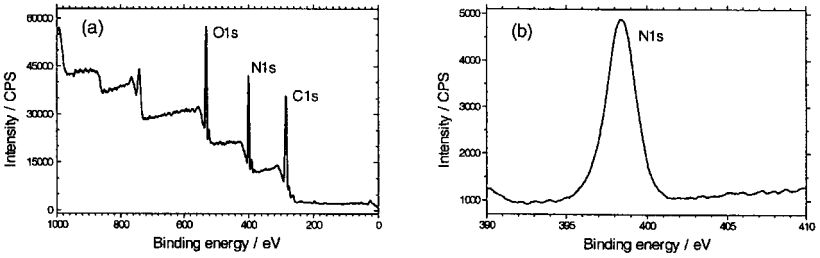
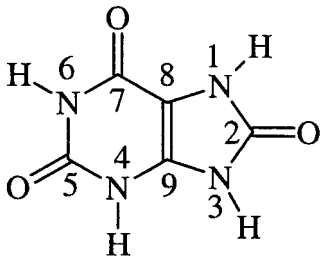


Figure 2. XPS survey scan for (a) uric acid stone S8, and the narrow scans of (b) N1s.

and energies of spin-orbital splitting for organic and inorganic nitrogen compounds,[16,23] such E_b values are largely characteristic of organic nitrogens N (−3), including amide, amino, amine, and so on. That is, the appearance of a low-energy component with $E_b = 399.5 \pm 0.2$ eV in the N1s band spectra in samples S8–S10 can be attributed to organic nitrogen atom in uric acid. In comparison, the E_b values of N (+5) in ammonium (NH_4^+X) and in other inorganic compounds are about 401 eV. For example, the E_b value of N1s in urolith S7 was 400.8 eV (Table 1). It is suggested that the N atom in urolith S7 existed as NH_4^+X species. Combined with the existence of phosphorus in S7 as shown in Tables 1 and 2, ammonium magnesium phosphate (NH_4MgPO_4) may have existed in this sample S7.

In conclusion, the XPS technique is useful for quick survey of stone type when epidemiology is changing. XPS can identify and locate various inorganic and organic species in urinary stones at the same time and to estimate the most dominant crystalline structure by studying element ratios by XPS. It can be used for a quantitative analysis of major, minor, and trace elements of very little samples in a single measurement. This technique has potential for elucidating the mechanism of stone formation and has particular significance in the prophylaxis of recurrence of urolithiasis in stone formers.



Scheme 2. Molecular structure of uric acid.

ACKNOWLEDGMENTS

This research work was supported by grants from the Key project of Guangdong Province (2001C31401), the Natural Science Foundation of Guangdong Province (013202, 980898), the Key Project of the Natural Science Foundation of China (20031010), and the Foundation of State Key Laboratory of Materials Chemistry and Applications of Peking University of China. We thank Dr. L. Kuan (Department of Urology, The First Affiliated Hospital of Medical College, Jinan University) for supply of urolith samples.

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Received March 7, 2003
Accepted August 31, 2004