

X-ray diffraction analysis of urinary tract stones

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Aim: To analyze urinary tract stones obtained in our clinic using various methods and to determine the spectrum of stone composition in the Eastern Anatolia Region, Turkey.

Materials and methods: A total of 300 stones were obtained at Atatürk University, Faculty of Medicine Urology Clinic through open surgery, percutaneous nephrolithotomy (PNL), ureterorenoscopy (URS), and extracorporeal shock-wave lithotripsy (ESWL) between 1 January 2005 and 30 December 2008. Stones were analyzed in the laboratory of Ankara General Directorate of Mineral Research Exploration using X-ray diffraction (XRD).

Results: It was found that 218 (72.7%) of the 300 stones were calcium oxalate (CaOx); 170 (56.7%) of which were calcium oxalate monohydrate (COM), 12 (4%) were calcium oxalate dehydrate (COD), and 36 (12%) were COM and COD combined stones; 23 (7.7%) were uric acid (UA), 6 (2%) were magnesium ammonium phosphate (MAP), 3 (1%) were dahllite (DAH/hydroxyl apatite), 2 (0.6%) were cystine (CYS) stones, and 34 (11.3%) were a combination of UA and COM stones. The remaining 14 (4.7%) stones were a combination of other stones.

Conclusion: The stone analysis study was carried out using the XRD method on 300 samples in the Eastern Anatolia Region, where the prevalence of urinary tract stones is relatively high. The analysis showed that 72.7% of all stones were CaOx stone and 56.7% were pure COM stones.

Key words: Urinary tract stones, x-ray diffraction, stone analysis

Üriner sistem taşlarını X-ray diffraction ile analizi

Amaç: Bu çalışmada, kliniğimizde çeşitli yöntemlerle elde edilen üriner sistem taşlarını analiz ederek, Türkiye'nin Doğu Anadolu bölgesinin taş bileşim spektrumunu ortaya koymayı amaçladık.

Yöntem ve gereç: Atatürk Üniversitesi Tıp Fakültesi Üroloji Kliniğinde 1 Ocak 2005 ile 30 Aralık 2008 tarihleri arasında; açık cerrahi, perkütan nefrolitotomi (PNL), üreterorenoskopi (URS) ve ekstrakorporel şok dalga litotripsi (ESWL) ile elde edilen total 300 taş değerlendirildi. Taşlar, Ankara Maden Tetkik ve Arama Genel Müdürlüğünde X-ray diffraction (XRD) yöntemi ile analiz edildi.

Bulgular: Analiz edilen 300 taşın; 218'i (% 72,7) kalsiyum oksalat (CaOx) taşı idi. CaOx taşlarının 170'i (% 56,7) kalsiyum oksalat monohidrat (COM), 12'si (% 4) kalsiyum oksalat dihidrat (COD) ve 36'sı (% 12) COM ve COD taş bileşimi idi. Analiz edilen taşlardan 23'ü (% 7,7) ürik asit (UA), 6'sı (% 2) magnezyum amonyum fosfat (MAP), 3'ü (% 1) dahllite (DAH/hidroksi apatit) ve 2'si (% 0,6) sistin (CYS) taşı idi. Otuz dört (% 11,3) taş UA ve COM bileşim taşı idi. Geri kalan 14 (% 4,7) taş, diğer bileşimlerden oluşmaktaydı.

Sonuç: Bu taş analiz çalışmasında, nispeten üriner sistem taş hastalığı prevalansı yüksek olan Doğu Anadolu Bölgesinde elde edilen 300 taş XRD ile analiz edildi. Analiz sonucu, taşların % 72,7'sinin CaOx taşı ve % 56,7'sinin pür COM taşı olduğu anlaşıldı.

Anahtar sözcükler: Üriner sistem taşı, X-ray diffraksiyon, taş analizi

Received: 29.09.2009 – Accepted: 09.03.2010

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Introduction

Urinary tract stone disease has been affecting humans for centuries, and it affects a quarter of the population in certain geographical regions and therefore cause important health problems. Many hereditary, nutritional, geographical, and infective etiologic factors may cause stone formation (1). While the risk of life-long urolithiasis in the western world is 10%-15%, this rate is 20%-25% in the Middle East (2). Without preventative treatment, the rate of recurrence is approximately 10.5% in 1 year, 33% in 5 years, and 50% in 10 years (3). Due to the high rate of recurrence, analysis of the obtained stones for the purpose of learning stone composition and preventing future intrusive procedures is of great importance. In stone analysis, XRD and infrared spectroscopy (IRS) are standard methods (4,5). Chemical methods are not reliable in stone analysis (5).

In the Eastern Anatolia Region, stone analysis can only be carried out by chemical methods. Since results obtained via this method are not reliable, it was necessary to change the method. For this reason, starting from 2005, we began to send the stones we obtained to the General Directorate of Mineral Research Exploration laboratory in Ankara for XRD analysis.

This study includes results of the first analysis we carried out using the XRD method.

Materials and methods

Urinary tract stones, which were obtained at Atatürk University, Faculty of Medicine Urology Clinic between 1 January 2005 and 30 December 2008, were analyzed in the laboratory of the General Directorate of Mineral Research Exploration in Ankara using the XRD method. The period between the collection and analysis of the stones varied between 3 weeks and 3 months. The stones were stored in a plastic bag without using any solution between removal and XRD-analysis. A total of 300 stones were analyzed; 120 of these stones were renal stones, 128 were ureteral stones, and 52 were bladder stones. One hundred of the stones were obtained with open surgery (pyelolithotomy, ureterolithotomy, or cystolithotomy), 154 were obtained with endoscopic

(PNL or URS) methods, and 46 were obtained by collection of stone fragments after ESWL. Although the number of patients who were treated with the ESWL method was quite high, since a sufficient amount of stone fragments could not be collected for detections, only the stones of 46 patients were obtained with this method.

The stones that were taken to the laboratory were pulverized and placed into glass sample cups. Samples were then placed into a Philips x-ray diffractometer with a nickel filter. Mineral determination was made from the diffraction patterns using the comparative Hanawalt method.

Results

In this study the number of adult males (m) was 201, the number of adult females (f) was 81, m/f ratio was 2.48, and the average age was 53 (range: 15-83). The number of child patients (<15 years of age) was 18. Ten of these were girls and 8 were boys. In this study, when COM, COD, UA, MAP, DAH, and CYS stones are considered as single crystalline components and pure stones, the pure stone rate was 72% (n = 216) and the rate of combined stones, including the components of these stones and others, was 28% (n = 84). Almost all (81/84) of the stone combinations contained COM crystal. As a result, the COM component was pure in 170 stones and a combination in 81 stones. The proportional expression of this is 83.6%.

Out of 300 stones obtained, 170 (56.7%) were found to be COM, 12 (4%) were COD, and 36 (12%) were COM+COD combination. Besides, 72.7% (n = 218) of all stones were CaOx stones. There were 34 (11.3%) COM+UA combinations, 23 UA (7.7%), 6 MAP (2%), 3 DAH (1%), and 2 CYS (0.6%) stones. The remaining 14 stones were a combination stones that were composed of 2 or more crystalline components.

In this study, only 3 DAH stones were detected to be pure calcium phosphate (CaP) stone and only 2 combined stones contained brushite crystal.

In this study there were only 6 pure infection stones (MAP), of which 5 (83.3%) were obtained from female patients. It was a significant finding that only 2 (0.6%) of 300 stones were CYS stones (Table 1).

When renal (n = 120) and ureteral (n = 128) stones were further analyzed as upper urinary tract (UUT) stones, it was found that 248 (82.6%) of the analyzed stones were UUT stones.

One hundred and ninety five (78.63%) of UUT stones were CaOx stones. The second most common stone type amongst upper urinary tract stones was the combined stone group that was composed of COM and UA components (Table 2).

It was found that 23 (44.23%) of 52 bladder stones were CaOx stone. UA stones ranked second among bladder stones. The rate of pure UA stones in the bladder was 26.92% and the total rate of bladder stones containing UA crystalline component was 46%. In addition, it was interesting that 60.8% (14/23) of pure UA stones were in the bladder (Table 3).

Of the 18 stones obtained from the patients in the pediatric age group, 13 were COM, 2 were COM+COD, 2 were COM+UA, and 1 was CYS stone. It was found that the stones in children were mainly (83.33%) CaOx stone.

Table 1. Stone types and rates (all stones).

Stone Type	Number (n)	Rate (%)
CaOx	218	72.7
COM	170	56.7
COD	12	4
COM+COD	36	12
UA	23	7.7
MAP	6	2
DAH	3	1
CYS	2	0.6
COM+UA	34	11.3
OTHER COMBINED	14	4.7
TOTAL	300	100%

CaOx: calcium oxalate, COM: calcium oxalate monohydrate, COD: calcium oxalate dehydrate, UA: uric acid, MAP: magnesium ammonium phosphate (struvite), DAH: dahllite, CYS: cystine.

Discussion

Medical treatments of stone disease should be based on the analysis of the stone. The composition of the stone should be known in order to make accurate decisions about the treatment procedure and

Table 2. Distribution and rates of upper urinary tract stones.

Stone Type	Number (n)	Rate (%)
CaOx	195	78.63
COM	157	
COD	10	
COM+COD	28	
UA	9	3.63
MAP	6	2.42
DAH	2	0.81
CYS	2	0.81
COM+UA	24	9.67
OTHER COMBINED	10	4.03
TOTAL	248	100%

CaOx: calcium oxalate, COM: calcium oxalate monohydrate, COD: calcium oxalate dehydrate, UA: uric acid, MAP: magnesium ammonium phosphate (struvite), DAH: dahllite, CYS: cystine.

Table 3. Distribution and rates of bladder stones.

Stone Type	Number	Rate (%)
CaOx	23	44.23
COM	13	
COD	2	
COM+COD	8	
UA	14	26.92
MAP	-	-
DAH	1	1.92
CYS	-	-
COM+UA	10	19.23
OTHER COMBINED	4	7.7
TOTAL	52	100%

CaOx: calcium oxalate, COM: calcium oxalate monohydrate, COD: calcium oxalate dehydrate, UA: uric acid, MAP: magnesium ammonium phosphate (struvite), DAH: dahllite, CYS: cystine.

to prevent recurrence (6-8). Due to the high error rate of chemical methods, for the analysis of urinary stones, physical methods, such as XRD and IRS, are recommended (9).

The crystal structure of urinary stones allows for XRD analysis and is accepted as the gold standard (10-14). This analysis is highly reliable due to its success in the definition of chemical structures composing the stone. The fact that this analysis can be applied to very small samples is another advantage

of the technique (9). In quality control analyses of 44 studies between 1980 and 2001, the XRD method produced the most accurate results for determining other components in combined stones. In this study it was found that the error in the detection of COM stones, which is the most common stone type in the urinary system, using the XRD method was only 13% (15). In recent years several publications have discussed the utilization of XRD and x-ray coherent scatter in the determination of the stone structure prior to surgery and in the analysis of the whole stone (4,14,16).

Because of the facts that different methods are used in stone analysis and sample numbers are highly variable, and because studies include upper urinary tract stones or all stones, it is difficult to accurately compare the reported results. However, many studies have reported a common finding that CaOx stones rank the first. On the other hand, when the existing literature on urinary tract stone diseases is reviewed, it is found that, depending on different regions and the etiologic factors related with stone formation, different stone structures emerged across the world (17). In various studies carried out in Western Europe and in the United States of America (18-22), it is observed that CaOx stones make up 50%-70% of all stones; and in studies carried out in India, located in the Middle of Far East (17,23,24), this rate exceeds 95%. Ahlawat et al. (24) reported that CaOx (COM/COD) stones, which were determined using XRD analysis of 435 urinary tract stones, made up 97% of all stones in Northern India. When our study is considered from this perspective, 72.7% of all stones, 78.63% of the upper urinary tract stones, and 44.23% of the bladder stones were CaOx stones. The results we obtained indicate that the distribution of stones in our region is similar to that observed in western societies. In a study that was carried out in Turkey using chemical analysis, it was reported that 55% of the stones were CaOx stones (25).

CaOx stones are composed of COM and COD crystals. COM is the most resistant structure in terms of thermodynamics, and is more common (>2:1) than COD in clinical stones (1,16,17,21). In our study the ratio of COM to COD was found to be 12. This ratio is quite high when compared to other findings reported in the literature. In the study by Herring (19),

the ratio of COD stones were higher than that of COM (40.9% vs. 31.4%). In our study, CaOx stones were categorized as COM, COD, and COM+COD. Ansari et al. (17) considered COM+COD stones separately from CaOx stones among other combined stones.

In many studies, the prevalence rate of pure CaP stones varies significantly between 6.2% and 28.9% (19-21,25). In our study the prevalence of CaP stones was low. As pure CaP stone, only 2 DAH (hydroxyl apatite) stones were found, and in 2 combined stones, brushite crystal was found. Similarly, there were only 2 stones in which CaOx and CaP stones were combined. This inconsistency with other studies mentioned above can be explained by the lower number of analyzed stone samples.

The prevalence of UA stones varies between 4.5% and 23%. More than 15% of urinary stones in Taiwan, Korea, and Saudi Arabia are comprised of UA stones (28). Ansari et al. (17) found that the rate of UA stones was only 0.95%. In our study, pure UA stones made up 7.7% of all stones; 3.63% of the UUT stones, and 26.92% of the bladder stones. In addition, when we consider COM and combined UA stones, 19% (57/300) of all stones contained UA. Our findings are generally consistent with other studies except that bladder stones in our study included a higher rate of UA stones (26.92%). Among urinary stones, the rate of MAP stones was reported to be between 9.3% and 21.5% in various studies (11,18,19,21,26). Ansari et al. reported 1.42% MAP stone rate (17). In our study, the rate of pure MAP stones was only 2% (6/300). In addition, one combined stone had a MAP component. This indicates that in our study the number of MAP stones is low, which is similar to the findings of Ansari et al. (17). On the other hand, the fact that almost all of the MAP stones are observed in women due to their tendency to infection is an expected result. Gault and Chafe (26) emphasized that 54% of MAP stones were observed in women.

CYS stones are rarely observed urinary tract stones. Prien and Frondel (11) reported that the prevalence of CYS stones was 3.8%. In many other studies (19,20,21,22,26) the prevalence of CYS stones is 1% or lower. Ansari et al. (17) did not detect any CYS stone among 1050 stones they analyzed using the XRD method. In our study only 2 (0.6%) pure CYS

stones were found. In previous studies carried out in our clinic, no CYS stones were detected (29,30). This indicates that CYS stones are rare in our region.

Different results were reported in previous studies of bladder stone analysis. In the study by Otnes (21), in which he analyzed 100 bladder stones using the XRD method, a mix stone composed of CaOx and CaP ranked first with a rate of 34%, and CaOx stones ranked fourth with a rate of 15%. Gault and Chafe (26) analyzed 1067 bladder stones and reported that CaOx stones ranked first with a rate of 65%. In that study it was interesting that the rate of bladder stones containing MAP stones was found to be 20%. In our study 44.23% (23/52) of the analyzed bladder stones were CaOx stones. The rate of pure UA stones in the bladder was 26.92% (14/52) and the total rate of bladder stones containing UA stone was 46.15%. Only one combined bladder stone contained a MAP component. In terms of the high rate of UA stones and low rate of MAP stones, the findings of our analyses regarding bladder stones appear to be inconsistent with the above mentioned studies.

It is known that in many regions of the world, childhood stone diseases are endemic. Studies indicate that childhood stone diseases are related to

nutritional disorders and the majority of the stones are mix stones composed of ammonium acid urate, CaOx, or a mixture of them (31-33). In our study the number of child patients was limited. However, the fact that 18 stones obtained from the patients in the pediatric age group did not contain ammonium acid urate and the majority of these stones (83.33%) contained only CaOx is inconsistent with the previous findings.

Conclusion

Currently advanced techniques can be used in the treatment of urinary tract stones. However, for the prevention of recurrence, stone analyses are still important.

In the present study, which analyzed 300 stones using the XRD method, it was found that 72.7% of all stones were CaOx stones and 56.7% were pure COM stones. When the results we obtained are compared with the data from the published literature, it is found that the prevalence of CaP and MAP stones is lower in our sample. However, for the complete specification of stone profile in our region, studies with larger samples should be carried out.

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