Crystalline Composition of Urinary Stones

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KEY WORDS

urinary stone ◗ crystals ◗ X-ray diffractometer

ABSTRACT

Introduction. By means of an X-ray diffractometer, it is possible to very precisely determine the composition of examined stones while identifying each kind of crystal. The objective of this paper is to make an *in vitro* assessment of the crystalline composition of urinary stones obtained during surgeries or those spontaneously excreted by the patients treated in the I and II Clinic of Urology of the Medical University in Łódź.
Material and method. The research was conducted with the use of X-ray diffractometers: Dron – 1 or D 5000 Siemens. One hundred eighty-eight urinary stones obtained from patients treated in the clinics were examined.
Results. The following crystals were found in the examined urinary stones: whewellite occurs in 97 (51.6%) stones, weddellite in 45 (23.9%), struvite in 82 (43.6%), apatite in 70 (37.2%), newberyite in 40 (21.2%), brushite in 34 (18.1%), bobierrite in 14 (7.4%), vitlokite in 7 (3.7%), uric acid in 12 (6.4%), ammonium acid urate in 1 (0.5%), calcium carbonate in 3 (1.6%), cystine and other sporadically occurring crystals were found in 0.6% to 1% of cases. Stones made of pure calcium oxalate constituted 18.1%. Oxalic stones with the additive of other crystals, although not containing any struvite, were found in 20.2% of cases, which in total makes 38% of the analyzed stones. Pure struvite stones constituted 5.3% and the ones with the additive of other phosphate crystals – 27.7%, which makes 33.0% in total. Uric acid stones constituted 5.3%, whereas with the additive of other crystals – 1.1%, which makes 6.4% in total. Cystine stones were found in 0.6% of cases. Mixed stones containing all kinds of crystals constituted 22.0%.
Conclusions. Diffractometric studies allow very precise determination of the composition of urinary stones. While using the crystalline structure as a criterion for dividing urinary stones, one cannot create any homogenous groups. On the basis of the conducted research, we divided urinary stones into oxalic, phosphate, uric acid, cystine, and mixed ones, the latter containing all possible kinds of crystals. The largest group is made of mixed stones, which constitute 55% of the deposits and combine infected stones without calcium oxalate and stones that are a mixture of struvite and calcium oxalate as well as other crystals. Another numerous group is made of oxalic stones – 38.3% of cases. Uric acid stones (6.4%) and cystine stones (0.6%) are less frequent. Based on the observations conducted it can be concluded that along with the increase in the number of crystals contained in a uric stone, the number of uric acid deposits decreases and the number of stones made of phosphate and mixed oxalic and phosphate crystals, often with the additive of struvite, grows.

INTRODUCTION

The composition of urinary stones can be determined by means of: chemical analysis, optical assessment of the crystals' structure, light microscope, diffractometric analysis, IR spectrometric analysis, thermographic methods, analysis with the use of electron diffraction, electron scanning microscope, and X-ray microanalysis. The ideal solution would be to use all the above-listed techniques, as each of them has some imperfections. The chemical method is time-consuming and if a sample of stones is small, it might turn out imprecise. Infrared spectrometry does not clearly reveal differences between whewellite and weddellite as well as between struvite and apatite. The X-ray diffractometer requires a constant minimum amount of powdered material for analysis. The electron microscope with a scanning attachment allows the registration of images of the surface and passages of the stones, however the elemental analysis of the surface layers of crystals contained in the examined stone is necessary in order to identify the crystals [1, 2, 3, 4].

All credit for the introduction and use of X-ray diffraction for the purpose of examining urinary stones goes to Jensen and later Prien and Frondel [5]. These studies were conducted in the 40's and 50's of the 20th century. The equipment used at this time allowed only one to three components contained in a stone to be revealed. The most frequently described crystals were: whewellite, weddellite, uric acid, apatite, struvite, brushite, and cystine. Along with the further development of studies, one started to describe crystals that are less frequently found in urinary stones, such as: zinc phosphate or aragonite (a variant of calcium carbonate). Today, with the use of an X-ray diffractometer, one can determine the composition of examined stones in a very precise way, identifying each type of crystal [6, 7].

The objective of the paper is to provide an assessment of the crystalline composition of urinary stones by means of an X-ray diffractometer and to present combinations, in which the crystals can occur while forming the examined deposits.

MATERIAL

One hundred eighty-eight urinary stones obtained from patients treated in the I and II Clinic of Urology at the Medical University of Łódź were examined. One hundred seventy of them were obtained from patients treated surgically with various techniques (PCNL, URSL, surgical treatment) and 18 came from out-patients who excreted the deposits spontaneously. All 188 stones had their

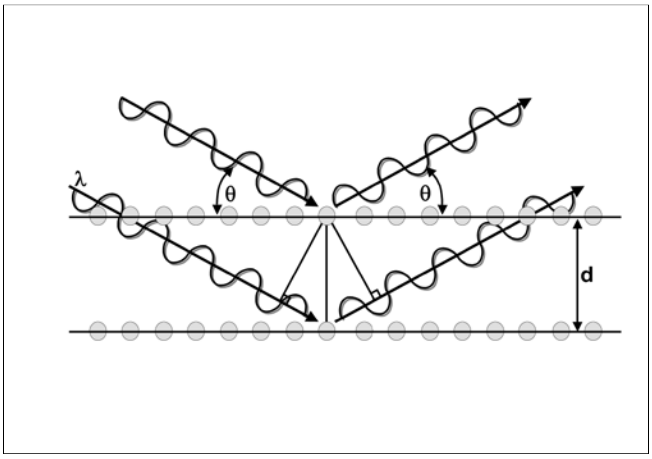

Fig. 1. The principle of emergence of diffraction on crystallographic net planes.

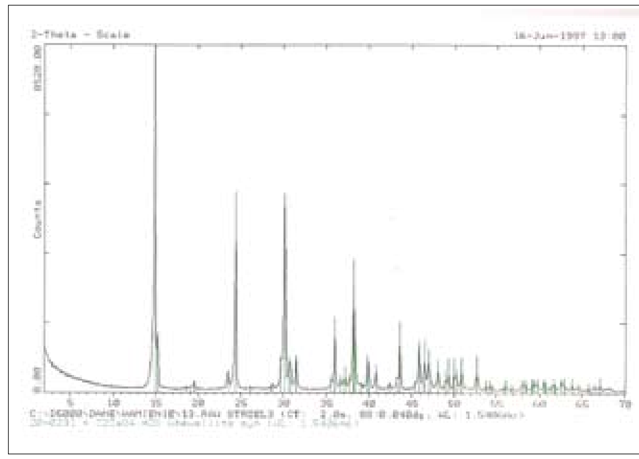

Fig. 2. Diffractometric diagram of a urinary stone made of whewellite (D 5000 Siemens X-ray diffractometer).

crystalline composition determined. This research was conducted in the Institute of Materials Science and Engineering at the Technical University of Łódź.

RESEARCH METHOD

If an X-ray beam is directed at a crystalline preparation then one of the phenomena that is going to take place will be the reflection of the X-rays from the crystallographic planes made of atoms which form the crystal. If certain conditions are met, the interference of the radiation is possible. In order to identify the phases that occur in the preparation, one makes use of the relation described by Bragg in the form of the following formula:

$n \lambda = 2*d*\sin\theta$ (Formula No. 1)

where:

n – is the reflection number

λ – X-ray wavelength

d – is the spacing between reflecting planes of the crystal

θ – reflection angle, the so-called Bragg's angle

The diagram of the phenomenon of interference at the planes of the crystal is demonstrated in Fig. 1.

Analysis of the formula (1) shows that in case of the specific X-ray wavelength, the family of planes characterized by a given inter-plane spacing, **d**, provides the interference of a given angle, θ. Therefore, if the wavelength and the angle at which interference occurs are known, the distance between the reflecting planes can be determined. This in turn is the basis for establishing the type of elementary cell and its parameters allowing identification of the examined phases.

In order to identify the phases occurring in the urinary stones, the D 5000 Siemens X-ray diffractometer (Karlsruhe, Germany) was used. The parameters of the research were as follows:

radiation – Co K_α

secondary graphite monochromator,

lamp working voltage – 30 kV,

lamp working amperage – 40 mA,

angle range examined: 2θ 10 – 140 deg.

RESULTS

One hundred eighty-eight urinary stones examined by means of X-ray diffractometers were divided into five groups depending on the number of crystals that form them and into five basic groups consistent with their chemical composition (Table 1). The stones consisting of one, two, three, four, or five and more kinds of crystals were assessed. The stones made of one type of crystal constituted 17% (32) of cases, stones made of two types of crystals – 33% (62), three types – 32.4% (31), four types – 14.9% (28), and five types – 2.7% (5). The most numerous groups contained the stones made of a combination of two or three crystals. The less numerous groups contained the stones made of one type of crystal or the combination of four types of crystals. The group of stones made of a combination of five and more crystals appears sporadically. It was found that along with the increase in the number of crystals, the number of stones made of phosphate crystals or phosphate and oxalic crystals also grows. Pure phosphate stones or these with the additive of phosphate crystals, excluding struvite, dominate in one- and two-component groups (Table 1).

The analysis of the groups of stones with regard to the number and type of crystals that form them showed that in one- and two-component groups, it is oxalic stones that dominate. In its pure crystalline form whewellite was found 11 times (Fig. 2), uric acid – 10 times (Fig. 3), struvite – 10 times (Fig. 4), and cystine – one time (Fig. 2). In three-, four- and five-component groups, it is struvite mixed stones with the additive of other phosphate crystals (Fig. 6) or mixed stones with the additive of phosphate, oxalic crystals, and uric acid that dominate. It was found that the stones made of calcium oxalate (whewellite and weddellite) constitute 18.1% of cases. Oxalic stones with the additive of other crystals and chemical compounds, excluding struvite, make 20.2% of cases. Altogether,

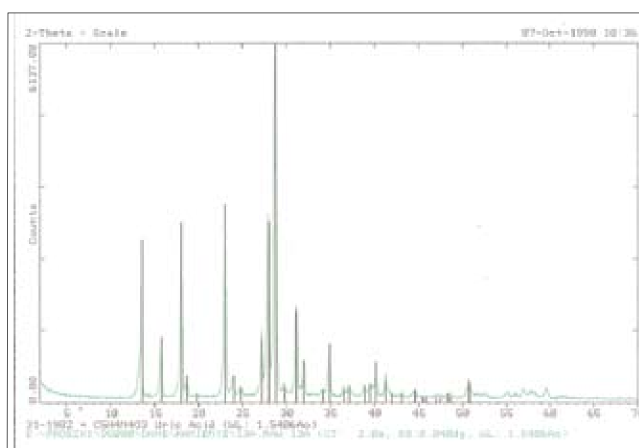

Fig. 3. Diffractometric diagram of a urinary stone made of uric acid (D 5000 Siemens X-ray diffractometer).

Table 1. Change in the mean International Index of Erectile Function (IIEF) one month and three months after placement.

Number of crystals	Type of urinary stones				
	Oxalic	Phosphate	Mixed	Uric acid stones	Cystine stones
1	whew11	Stru.10	0	ur. ac 10	cys. 1
2	whew, wed. 23 whew, bru. 4 whew, apa. 4 whew, vit. 1 whew, ur. ac 1 whew, bob. 1 whew, new. 1 whew, cal. car 1 whew, ac. amm. ur. 1	Stru. apa. 9 stru. new. 3 stru, ur. ac. 3 apa, bob. 1 apa, vit. 1 apa, bru. 1	whew. stru. 4	ur. ac, new. 1 ur. ac, cal. ur. 1	
3	whew, wed, apa. 5 whew, wed, bru. 2 whew, apa, bru. 2 whew, wed, new. 3 whew, new, bob. 1 whew, eps, cal. phos. 1 whew, apa, ch. apa. 1 whew, wed, ur. ac 1 whew, cal. phos, 6xH_2O ac. mag. phos. 1	Stru, apa, new. 9 stru, apa, bru. 6 stru, apa, vit. 3 stru, apa, bob. 2 stru, new, bru. 1 stru, new, cal. car 1 stru, new, ur. ac. 1 stru, new, 6xH_2O mag- amon. phos 1 apa, vit, new. 1	whew, wed, stru. 7 whew, new, stru. 3 whew, bru, stru 1 stru, bru, wed. 3 stru, apa, wed. 4 stru, ur. ac, wed. 1 stru, whew, hyd. flu. apa. 1		
4	whew, wed, apa, bob. 1 whew, wed, bru, new. 1 whew, wed, apa, bru. 2 whew, apa, ur. ac, bru. 1 whew, wed, ur. ac, bru. 1	Stru, apa, bru, bob. 4 stru, apa, bru, new. 2 stru, apa, new, bob. 1 stru, apa, bru, cal. car. 1	stru, new, whew, wed, 5 stru, apa, whew, wed, 4 stru, bru, whew, wed. 1 stru, new, bru, wed. 1 stru, apa, bob, wed. 1 stru, apa, bru, whew. 1 stru, whew, wed, hyd. flu. apa. 1		
5	whew, wed, new, bru, bob. 1	Stru, hyd. apa, mag. phos, 8xH_2O mag. phos, sod. mag. phos, H_2O mag. phos, eps, Sio. 1	Stru, apa, new, whew, wed. 1 Stru, new, ur. ac, whew, wed. 1 Stru, apa, bru, bob, whew. 1		

Description of abbreviations: whew – whewellite, wed – weddellite, stru – struvite, apa – apatite, ch. apa – chlor-apatite, hyd. flu. apa – hydroxy fluoroxy apatite, new – newberyite, bru – brushite, bob – bobierrite, vit – vitlokite, ur. ac – uric acid, ac. amm. ur – acid ammonium urate, cal. ur – calcium urate, cys – cystine, eps – epsomite, sio – siogrenite, 6xH_2O mag. phos – hexahydrate magnesium phosphate, 6xH_2O mag-amon. phos – hexahydrate magnesium-ammonium phosphate, cal. phos – calcium phosphate, mag. phos – magnesium phosphate, 8xH_2O mag. phos – octahydrate magnesium phosphate, sod. mag. phos – sodium magnesium phosphate, H_2O mag. phos – monohydrate magnesium phosphate

the group of oxalic stones constitutes 38.3% of examined deposits. Infected stones made of struvite constitute 5.3% of cases, whereas the ones made of struvite with the additive of other crystals, excluding phosphate crystals, constitute 27.7% of examined deposits. The group of struvite stones without the additive of oxalic crystals encompasses the deposits formed in the environment of infected urine, which constitute 33.0% of examined stones. Pure uric acid was found in 5.3% of stones. In the case of 1.1% of stones containing uric acid, there was newberyite or calcium urate registered. In total, the group of uric acid stones constitutes 6.4% of deposits. Cystine as the only component of stones was found in 0.6% of stones, i.e. in one deposit. Mixed stones constitute 22% of the whole examined sample and they are made of: oxalates, phosphates, uric acid and other sporadically occurring chemical compounds (Tables 1 and 2).

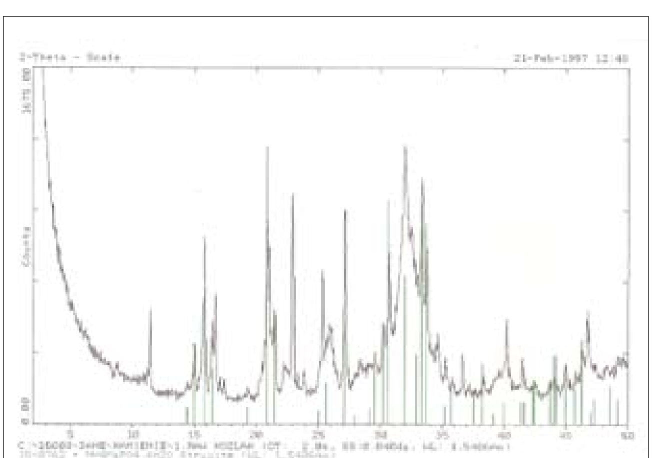

Fig. 4. Diffractometric diagram of a urinary stone made of struvite (D 5000 Siemens X-ray diffractometer).

Diffractometric diagram of the urinary stone made of hydroxyapatite, struvite, magnesium phosphate, octahydrate magnesium phosphate, sodium magnesium phosphate, monohydrate calcium phosphate, epsomite, siogrenite (D 5000 Siemens X-ray diffractometer).

During the assessment of the frequency of occurrence of crystals in the urinary stones regardless of the type of deposit, it was found that the most frequently registered crystals are: whewellite in 51.6%

Table 2. Type of urinary stones and crystals that form them.

Type of urinary stones	Types of crystals	Number and % of stones n = 188	Total
Oxalic stones	Whewellite	11/5.9%	72/38.3%
	Whewellite/Weddellite	23/12.2%	
	Oxalates and phosphates without struvite	38/20.2%	
Infected/struvite stones	Struvite	10/5.3%	62/33.0%
	Struvite and other phosphates	52/27.7%	
Urate stones	Uric acid	10/5.3%	12/6.4%
	Uric acid and other crystals	2/1.1%	
Cystine stones	Cystine	1/0.6%	1/0.6%
Mixed stones	Oxalic struvite stones and other stones	41/22.0%	41/22.0%
Total		188/100%	188/100%

of stones, struvite in 43.6% and apatite in 37.2%. Weddellite (23%), brushite (18.1%), newberyite (21.2%), uric acid (6.4%), or bobierrite (7.4%) occur less frequently. Vitlokite, calcium carbonate, cystine, calcium urate, or ammonium acid urate occur sporadically. In six urinary stones, the following crystals or chemical compounds occur individually: – hydroxyfluoroxyapatite, epsomite, hexahydrate magnesium phosphate, chlor-apatite, magnesium phosphate, sodium magnesium phosphate, monohydrate calcium phosphate, siogrenite, and hexahydrate potassium magnesium phosphate (Table 3).

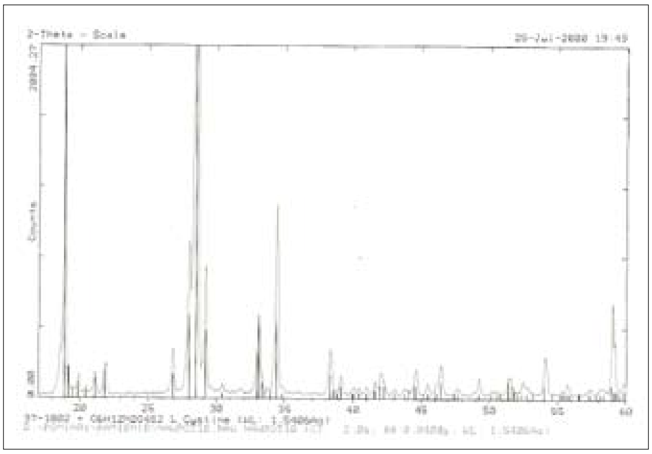

Fig. 5. Diffractometric diagram of a urinary stone made of cystine (D 5000 Siemens X-ray diffractometer).

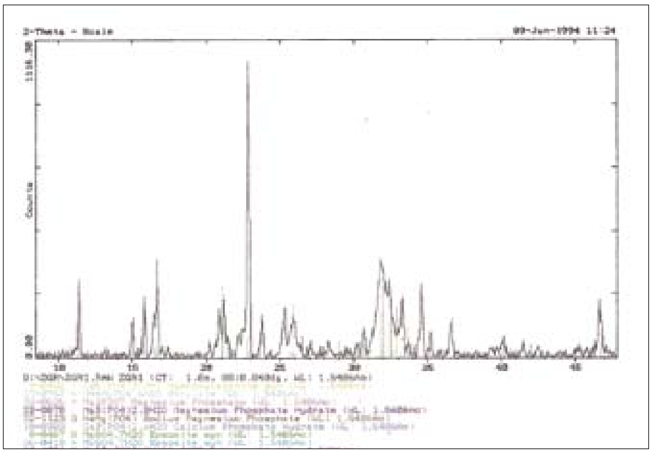

Fig. 6. Urinary stone of complex crystalline composition (D 5000 Siemens X-ray diffractometer).

DISCUSSION

The possibility to conduct diffractometric analysis of urinary stones allowed for a very precise assessment of the frequency of occurrence of various types of crystals and their combinations in the examined deposits. Pure calcium oxalate was found in 31 (18.1%) out of 188 examined stones. However, the ones that ad-

Table 3. Frequency of occurrence of crystals in 188 urinary stones.

Crystal name	No. of stones containing the crystal	%
whewellite	97	51.6
weddellite	45	23.9
struvite	82	43.6
apatite	70	37.2
newberyite	40	21.2
brushite	34	18.1
bobierrite	14	7.4
uric acid	12	6.4
vitlokite	7	3.4
acid ammonium urate	1	0.5
calcium carbonate	3	1.6
calcium urate	1	0.5
cystine	1	0.6
calcium phosphate	1	0.5
hydroxyapatite	1	0.5
chlor-apatite	1	0.5
hydroxyfluoroxyapatite	2	1.1
hexahydrate acid magnesium phosphate	1	0.5
hexahydrate ammonium magnesium phosphate	1	0.5
siogrenite	1	0.5
magnesium phosphate	1	0.5
sodium magnesium phosphate	1	0.5
monohydrate calcium phosphate	1	0.5
octahydrate magnesium phosphate	1	0.5

ditionally contain the additive of other crystals, except struvite typical of infected calculosis, should also be numbered among the group of oxalic stones. In this case, the group of oxalic stones is expanded by 38 (20.2%) stones and contains 38.3% (72) of all the examined deposits. Szpila [8] states that in his material, monohydrate calcium oxalate occurs in 27% of cases. Balla registered the crystals of whewellite in 46% of examined stones [9]. Similar analysis conducted in Great Britain revealed 44%, in Germany – 47%, in the Republic of South Africa – 83%, and in the United States – 31% [10].

Struvite stones formed in the infected urine were found in 5.3% of cases, whereas the ones with the additive of other crystals without calcium phosphate in 27.7%. In total, the group of stones that can be formed in infected urine constitutes 33% of examined deposits. The results demonstrated by other researchers are as follows: 32.0% in Great Britain, 28.6% in Germany, 5.0% in the Republic of South Africa and 26.0% in the United States [10]. While comparing the frequency of occurrence of stones made of pure struvite, we see that it amounts to 14.0% in Great Britain, 12.0% in Germany, 2% in the Republic of South Africa, and 15.0% in the United States [10]. Szpila et al. reports that struvite stones made only 1.8% of his material [8]. Such a high percentage of struvite stones in our sample suggests frequent infections of patients' urinary tracts in the analyzed material. In the presented material, uric acid stones were found in 6.4% of cases, which is a higher percentage than in the event of the results presented by Szpila – 3.8% or scientists from Great Britain – 3.0%, but lower than in case of the United States – 9.0% and Germany – 13.0% [8, 10]. Cystine was found in one case which constituted 0.5% of stones. The most interesting group, but on the other hand the most difficult one in terms of making divisions, encompasses mixed stones made of various kinds of crystals as oxalates, struvite, other phosphates, and uric acid take part in their formation. In our material, this group constitutes 22.0% (41) of stones. Balla reports 15.7% and Sperrin – 26% in case of the US [9, 10]. However, if one counts the group of deposits made of struvite and other phosphates, excluding pure struvite stones, among the mixed stones, it will amount to 49.5% of cases, which is 93 deposits. This group will resemble similar ones reported by Ohkawa (56.8%) and Takasaki (50.8%) [11, 12]. The comparison with the first diffractometer analysis of urinary stones conducted by Prien showed the similarity in terms of occurrence of oxalic stones (36.2% in Prien's material, 38.3% in this material) and uric stones (6.1% in Prien's material, 6.4% in this material) [5]. If we aggregate all the stones containing struvite, apatite, other phosphates, and calcium oxalate, this group will amount to 50.5% of deposits in Prien's material and 55.0% in this one. One can see that it is difficult to create a perfect division of urinary stones. Leusman suggested the division of urinary stones into 5 classes: calcium stones, infected stones, uric acid stones, cystine stones, and xanthine stones [13]. Parks et al. divided urinary stones into some other groups [14]. The Park's groups encompassed mixed stones containing various percentages of calcium oxalate, phosphates, and other crystals. This division proves that the majority of urinary stones are a combination of different crystals occurring in smaller and bigger groups. Reveillaud et al. divided the examined stones into eight morphological types based on the research conducted by means of IR spectrophotometer [15].

The use of modern X-ray diffractometers allows very precise determination of the crystalline composition of the examined stone. Results regarding crystalline composition obtained in this way cause a lot of problems for researchers. As one can see, local conditions in the urinary system as well as medicines applied and patient's diet can influence both, the type of crystals that are formed in the stones and the number of their combinations. This makes it impossible to create large groups of urinary stones of the same crystalline composition. This fact is also proven by the multitude of crystals and their combinations in this study. However, if we divide the stones into some basic chemical groups, we will find that calcium oxalate crystals dominate the stones containing one or two types of crystals. In the groups of stones in which the number of crystals is greater, it is struvite or mixed oxalate-phosphate stones that dominate. The situation is similar with regard to the stones made of pure uric acid and cystine; they usually occur in one-component stones and sporadically in multi-component ones. It should be stressed that about 30% of stones have a monocrystalline composition and Brien et al. points to this fact as well. In our material, there are 17.1% of stones made of one type of crystals and if we add the stones made of whewellite and weddellite (as the deposits made of calcium oxalate) to this group, it will expand to 29.3% and become comparable to the one reported by Brien [16].

CONCLUSIONS

Diffractometric studies allow to precise determination of the composition of urinary stones. While using the crystalline structure as a criterion for dividing urinary stones, one cannot create any homogenous groups. On the basis of the conducted research, we divided urinary stones into oxalate, phosphate, uric acid, cystine, and mixed ones, the latter containing all possible kinds of crystals. The largest group is made of mixed stones, which constitute 55% of all deposits and combine infected stones without calcium oxalate and stones that are a mixture of struvite and calcium oxalate as well as other crystals. Another numerous group is made of oxalic stones – 38.3% of cases. Uric acid stones (6.4%) and cystine stones (0.6%) are less frequent. On the basis of the conducted observations, it can be concluded that along with the increase in the number of crystals contained in an uric stone, the number of uric acid deposits decreases, whereas the number of stones made of phosphate and mixed oxalate and phosphate crystals, often with the additive of struvite, grows.

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