PECULIARITIES OF THE COMPARATIVE METALLOGRAMS OF THE UROCONCREMENTS HAVING URATES AS DOMINANT COMPONENT AND PHOSPHATES AS DOMINANT COMPONENT

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ABSTRACT

Investigations were made on uroconcrements collected from two groups of subjects (patients) with kidney stones and admitted in the hospital. In the first step, using Fourier Transformed Infrared Spectroscopy (FT-IR) the types of uroconcrements were defined. Further on, a limited number of uroconcrements were analyzed by means of atomic absorption spectroscopy (AAS) in order to determine the concentration of the some alkaline (Na, K) and alkaline-earth (Ca, Mg) metals in their composition. From the first group only the uroconcrements having urates as dominant components and from the second group only the uroconcrements having phosphates as dominant components were selected. The comparison of the obtained metallograms revealed aspects about the types of lithiasis and their specificity.

Key words : metallograms, urates lithiasis and phosphates lithiasis

INTRODUCTION

Metals are important components of the human organism which are neither produced nor destroyed by the organism and are present in our environment, i.e. food, water, air, soil.

In the etiopathogeny of urolithiasis metals play a key role and may intervene either indirectly as effectors (inhibitors-activators) of metabolic processes, or directly as substituents engaged in competing interactions owing to the difference in the solubility products of oxalic, phosphatic salts etc. (Berg et al., 1990; Haraguchi, 2004)

The urolithogenesis begins with the appearance of so-called "starters" or "primers" resulted by precipitative mechanisms, involving the presence of a single specific anion (e.g. urates, phosphates, oxalates) or coprecipitative ones involving two or more anions. These anionic (organic and inorganic) compounds may bond with: metallic ions; non-metallic ions (NH_4^+); non-ionic compounds.

MATERIALS AND METHODS

The analytical investigations were made on the surgically removed or spontaneously eliminated urinary calculi collected from two groups of subjects (patients) admitted in the University Clinic of Urology Timişoara in different periods. By means of Fourier Transformed Infrared Spectroscopy (FT-IR), using a JASCO FT-IR/410 type apparatus (Channa et al., 2007) in the 400-4000 cm^{-1} wavenumber range at 4 cm^{-1} resolution, the qualitative composition of each calculi was determined. In a preliminary stage of the study the standard IR spectra of the chemically pure compounds present in calculi (organic - oxalic acid, uric acid, xanthine, cystine, cholesterol and inorganic - phosphates, carbonates) were recorded in order to establish the type of urolithiasis.

From the first group of 276 subjects there were selected only the uroconcrements having urates as dominant component (noted n_u) - 84 cases. From the second group of 237 subjects there were selected only the uroconcrements having phosphates as dominant component (noted n_p) – 133 cases.

The selected uroconcrements were analyzed by means of atomic absorption spectroscopy (AAS) and the concentrations of the following metals were determined : Na, K, Ca, Mg. Investigations were performed by a PYE UNICAM series Sp 1900 spectrophotometer in the spectral range of λ = 189-855 nm. The obtained analytical data were processed statistically : mean values (X) and standard deviations (SD) have been calculated for each metal (expressed as μg/g calculi).

RESULTS AND DISCUSSIONS

The human urine is a metastable solution which contains beside nitrogenous compounds, protein, polysaccharides, organic acids and also anions and inorganic cations (Na, K, Ca, Mg, Zn, Cu, Mn, Fe). These ions play an important role in the lithogenic processes. The concentration of these elements may vary due to various factors like: the solubility differences of the compounds, the pH and the molality of the medium as well as to the morphofunctional status of the kidney and urinary tract. Between the organic and inorganic compounds some precipitative and/or co-precipitative processes may occur. These processes are at the core of the uroconcrements nucleation due to the appearance of the so called "primers" or "starters" (Garban et al., 1998; Avacovici and Garban, 2007).

Metals are present in uroconcrements as an outcome of the fact that they are also present in urine. Berg et al. (1990) found that the urine of the patients with calculosis has higher concentration of Ca and Mg, while the concentrations of Na and K display only minor variations compared to the control group.

In the scientific literature there are few systematic studies on the distributions of metals in uroconcrements. Most of these researches are focused on the concentration of metals related with the age and sex of the patient, or with the areal in which they reside (Yamamoto et al., 1987; Hesse et al., 1993; Drăgan et al., 2000; Schubert, 2006).

A small number of scientific papers have an in depth approach regarding the qualitative composition of uroconcrements, i.e. the type of urolithiasis and the distribution of metal elements related to the type of urolithiasis (Joost şi Tessadri, 1987; Paluszkiewicz et al., 1990).

The FT-IR spectrum reveals two categories of bands: main spectral bands – characteristic for the standard substance and diagnose bands – that are used for the evaluation of components. For uric acid and urates the values are 3015 cm^{-1}, 1305 cm^{-1}, 1220 cm^{-1}, 1120 cm^{-1}, 1025 cm^{-1}, 705 cm^{-1}, 575 cm^{-1}, 475 cm^{-1} and for phosphates the values are 3420 cm^{-1}, 1470 cm^{-1}, 1430 cm^{-1}, 1055 cm^{-1}, 765 cm^{-1} (Khand et al., 1991).

Using the AAS method, the metal concentrations of the simple and mixed uroconcrements with urates and phosphates were determined and their values have been expressed as μg / g calculi in order to confer a unitary way for evaluation.

The results concerning the concentration alkaline and alkaline-earth metals are presented in Tabel 1 for the uroconcrements having urates as dominant component and in Table 2 for uroconcrements having phosphates as dominant component (Drăgan et al., 2000).

The obtained values of studied alkaline-earth metals (Ca, Mg) are comparable with those of authors like Bellanato et al. (1987) and Joost and Tessadri (1987).

If in the urates lithiasis the dominant metals are Ca and Na in those with phosphates prevail Ca and Mg. This is due to the electrochemical bondings that lead to tricalcic phosphate and ammonium-magnesium phosphates. All these ions take part in the lithogenic process.

Table 1. Alkaline and alkaline-earth metals in uroconcrements having urates as dominant component

Types of urolithiasis		Concentration of metals (μg/g calculus)							
		Na		K		Ca		Mg	
		n_u	X ± SD	n_u	X ± SD	n_u	X ± SD	n_u	X ± SD
Simple	Urate (U)	48	593.16±262.07	48	198.86±101.23	48	638.36±281.56	48	142.61 ± 93.09
Mixte	Urate-Oxalate (U-O)	9	1319.23±418.51	9	338.75±139.84	9	121 416.00±47.200.00	9	376.14±102.19
	Oxalate-Urate (O-U)	19	1748.14±586.12	19	491.13±187.02	19	187 342.00±52 814.00	19	412.93±27.31
	Oxalate-Urate- Phosphate (O-U-P)	8	2251.18±521.16	8	946.51±113.67	8	191 253.00±88 502.00	8	34350.40 ± 4985.70

Note: n- number of cases; $\bar{X}$ – mean values ; SD – standard deviation.

Table 2. Alkaline and alkaline-earth metals metals in uroconcrements having phosphates as dominant component

Types of urolithiasis		Concentration of metals (μg/g calculus)							
		Na		K		Ca		Mg	
		n_p	X ± SD	n_p	X ± SD	n_p	X ± SD	n_p	X ± SD
Simple	Phosphate (P)	42	9885.78 ± 426.51	42	2397.46 ± 1017.84	42	118 967.21 ± 57416.61	42	57218.61 ± 2141.93
Mixte	Oxalate- Phosphate (O-P)	44	5312.79 ± 187.31	44	994.41 ± 141.82	44	194 126,00 ± 29863.20	44	5347.51 ± 1844.78
	Phosphate-Oxalate(P-O)	21	13496,23 ± 3862.49	21	2798.82 ± 987.71	21	162 014.23 ± 79167.71	21	34530.40 ± 4985.70
	Oxalate-Phosphate-Urate (O-P-U)	6	2241.79 ± 513.53	6	972.93 ± 68.13	6	192 816.80 ± 89601.90	6	938.41 ± 496.83

Note: n- number of cases; $\bar{X}$ – mean values; SD – standard deviation.

CONCLUSIONS

1. By means of Fourier transformed infrared spectroscopy (FT-IR) there were established the types of urolithiasis. The metallic composition of the simple and mixed uroconcrements having urates and phosphates as dominant components have been determined by means of atomic absorption spectroscopy (AAS).
2. Metallograms of alkaline and alkaline-earth metals concentration in the uroconcrements having urates as dominant component showed a decrease in the series:

Simple lithiasis	Ca > Na > K > Mg
Binary lithiasis	Ca > Na > Mg > K
Ternary lithiasis	Ca > Mg > Na > K

3. Alkaline and alkaline-earth metals concentration in the uroconcrements having phosphates as dominant component decreased in the series:

Simple lithiasis	Ca > Mg > Na > K
Binary lithiasis	Ca > Mg > Na > K
Ternary lithiasis	Ca > Na > K > Mg

Note. This paper is dedicated „in memoriam" to Prof. Dr. Petru Drăgan (February2, 1932 – November 12, 200) - head of the University Clinic of Urology Timişoara, Faculty of Medicine, University of Medicine and Pharmacy "Dr. Victor Babeş" Timişoara (1987-2005)

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