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Concentration and Distribution of Some Minor and Trace Elements in Urinary Tract Stones: A Preliminary Study

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Introduction. Stone analysis has been directed mainly towards establishing and confirming the presence of calcium phosphates, oxalates and a variety of less common constituents such as cystine. Routinely analyses of this sort can be undertaken by the hospital laboratory (10). More sophisticated techniques such as X-ray crystallography have been applied to allow the various forms of phosphate, oxalate and urate to be distinguished e. g. the mono and dihydrates of calcium oxalate (6, 7). The present study using in vivo neutron activation analysis has been aimed at the elucidation of the constitution of urinary tract stones in terms of, not only the major elements, but also the minor and trace element contents.

Key words: Urinary stones - Trace elements - Neutron activation analysis.

METHODS

Sampling

Stones which had been removed or voided from five patients, three male and two female, were analysed biochemically to establish their compound type. Three calculi consisted of pure calcium oxalate and two of calcium phosphate. One half of each stone was retained for in vivo neutron activitation analysis.

Activation analysis

Samples ranging from 0.7 to 1.1 g of material were taken from the stones using polythene instruments to prevent metal contamination (8). After powdering in an agate mortar and homogenizing they were activated by irradiation in the Universities Training Reactor (East Kilbride) at a neutron flux of 3×10^{12} n sec^{-1} cm^{-2}. Two types of irradiation were carried out, one of 1 minute duration to activate elements with short-lived radioactive products and one of 50 hours to activate longer lived components. Each elements produced characteristic gamma rays resulting in complex spectra from each of the samples. These spectra were determined and resolved using a 20 cm^3 Ge/Li semiconductor detector with 2048 multichannel analysis (1). Concentrations of the elements either in % or $\mu g\ g^{-1}$ dry weight were calculated by comparison with standards designed to simulate the calculus material. These standards contained known amounts of the elements and were activated and determined in the same way. The short irradiation procedure enabled sodium, magnesium, chlorine, potassium and iodine to be determined and the longer procedure calcium, iron, cobalt, selenium, rubidium and caesium (2).

In the case of the phosphate stones these had a layered structure making it possible to remove samples from different regions and examine the distribution of the elements throughout the structure. The oxalate specimens were more homogeneous with no obvious structure except in one case where white and yellow components could be distinguished by their different crystalline characteristics. These components were hand separated and sampled for analysis. Duplicate samples of material were taken and analysed in all the cases described.

RESULTS

Table 1 shows the concentrations and distribution of the major and minor elements found in the

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Table 1. Concentrations of major and minor elements in renal stones

Stone	Concentration (% dry weight)									
	Phosphate type						Oxalate type			
	1			2			3		4	5
	Central layer	Middle layer	Outer layer	Central layer	Middle layer	Outer layer	White fraction	Yellow fraction		
Na	1.0	0.88	1.3	0.64	0.68	0.64	(1.21)	0.75	0.35	0.18
Mg	5.3	6.2	4.0	6.1	5.1	5.5	(1.15)	0.41	0.15	0.074
Cl	0.026	0.027	0.030	0.10	0.16	0.15	(0.068)	0.079	0.21	0.072
K	0.43	0.41	0.40	0.34	0.31	0.68	-	ND	ND	ND
Ca	12.4	12.3	19.4	8.3	11.4	13.3	(29.7)	29.6	29.7	29.8
Zn	0.32	0.029	0.054	0.037	0.026	0.078	0.183	0.136	0.042	0.012

Values in parentheses are for homogenates of whole stone material.
ND = not detected
- = not determined

Table 2. Concentrations of trace elements in renal stones

Stone	Concentration (μg g^{-1} dry weight)									
	Phosphate type						Oxalate type			
	1			2			3		4	5
	Central layer	Middle layer	Outer layer	Central layer	Middle layer	Outer layer	White fraction	Yellow fraction		
Fe	4.5	5.0	5.5	10	ND	15	ND	34	120	ND
Co	0.025	ND	0.020	0.09	0.28	0.51	ND	0.015	0.05	0.007
Se	ND	ND	ND	ND	ND	ND	ND	0.31	0.5	0.14
Rb	9.3	12.3	11.6	10.5	8.6	8.4	2.8	0.8	1.0	ND
I	3.3	9.2	9.5	62	83	72	ND	ND	96	ND
Cs	0.049	0.084	0.033	0.076	ND	0.048	ND	ND	0.02	ND

ND = not detected

stones. The results are mean values of the duplicate samples and overal errors are between ± 7% and ± 10% for all the determinations except potassium for which it is ± 20%.

Trace element concentrations and distribution are given in Table 2 where similarly the mean of duplicate determinations is quoted and the errors are of the order of ± 20% in all cases except rubidium which is ± 10%. Where an element is below the limit of detection this is indicated.

DISCUSSION

Comparing the specimens, there appear to be some significant differences which are worthy of comment. Magnesium and potassium are present in significantly higher concentrations in the phosphate specimens. The limit of detection for potassium in the oxalate cases is approximately 0.1%. Sodium has relatively low values in two of the oxalate stones. Chlorine and zinc show variation between specimens but definite trends are difficult to identify.

For two of the trace elements (Table 2) there are significant differences between the stone types. Rubidium is consistently present at higher levels in the phosphate stones (~ 10 μg g^{-1}) than in the oxalate stones (~ 2 μg g^{-1}) and whereas selenium is absent from the former, small amounts are present in the latter. (The estimated limit of detection for selenium is approximately 0.05 μg g^{-1}). Of the other trace elements determined iron, cobalt and iodine are variable in occurrence while caesium has a tendency to be associated mor with phosphate type stones in a similar fashion tu rubidium. In addition to these elements the presence of others was also detected qualitatively. Thus traces of antimony occurred in four of the specimens, scandium was observed in two of the oxalate stones but none of the phosphate, strontium was observed in the phosphates but not the oxalates and there was evidence of mercury in one of the oxalate stones.

Considering the distribution of elements throughout the stone structures most detail was obtained in the case of the phosphatic specimens. All the elements exhibited more or less even distributions except for cobalt and zinc which showed some variability.

Using activation analysis it is possible to examine the elemental composition of individual stones. The method is also useful for studies of the variation of concentration of elements within a stone as suitable small samples of material can easily be selected and analysed without prior chemical treatment. Stone material is soft enough to be divided for analysis using only plastic instruments thus preventing metal contamination.

Although only a small number of specimens has been examined in this study some conclusions can be drawn. It is probable that the minor and trace element constitution is a reflection of urine composition over the period of stone formation. An indication that a particular element had a significant role in stone formation or development would perhaps have been the occurrence of an unusual concentration at the centre of a specimen or in a particular layer. This occurs in one of the phosphate stones where Zn has a much higher concentration in the central region than in the outer layers.

An interesting and unexpected finding is that potassium is easily detected in phosphate stones but less so in oxalate. A similar difference exists with rubidium and caesium. In the case of sodium there is also a suggestion that the concentration is lower in the oxalate stones although more specimens would need to be analysed to confirm this. Thus it appears that the alkali metals as a group tend to have lower concentrations in the oxalate stones. It would therefore seem logical that in urinalysis of a stone former the elements sodium, potassium, rubidium and caesium should be included in addition to more commonly measured elements such as calcium and magnesium (9) and their relative concentrations might be found to be significant in phosphatic and oxalate stone formers. This is currently being investigated. In an analysis of bladder calculi it was recorded that rubidium was found in concentrations greater than would be expected and has been suggested as being a possible lithogenic factor along with zinc (4). Already there has been evidence that the ratios of magnesium to calcium (5) and zinc to calcium (3) are significant factors in the urine of stone formers. Perhaps the elements occurring at tracer levels, particularly the alkali metals, could have an important role in stone formation.

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