



PHYSICAL CHARACTERISTICS, QUALITATIVE AND QUANTITATIVE ANALYSIS OF URINARY STONES (PATHARI)

SUMAN PARIHAR^a, PRASOON HADA* and SNEH SHARMA

Deptt. of Chemistry, Govt. P. G. College, DAUSA (Raj.) INDIA

^aGeetanjali Medical College & Shrinath Hospital, UDAIPUR (Raj.) INDIA

ABSTRACT

The knowledge of chemical composition of stones (pathari) helps in understanding the mechanism of their formation and thereby providing guidelines for proper medical management of pathari disease. Keeping in view these facts, their weight, physical characteristics, qualitative and quantitative analysis of 58 stones was carried out. Salient features of qualitative analysis were; (a) presence of calcium and oxalate in all stones, (b) presence of ammonium in 96.5% of stones, which indicated either presence of struvite (magnesium ammonium phosphate) or ammonium acid urate and (c) absence of cystine in all the stones. Qualitatively, oxalate was the major constituent of the stone (30.18 + 11.96 g %). Urine chemistry and crystalluria of these stone formers (SF) was also analysed. No relationship was observed between the urine chemistry and chemical analysis of stones. Crystalluria was studied in urine samples from stone formers at the time of admission, just before operation and after seven days of operation. There was decrease in crystalluria in the urine samples after the operation. The weight, shape, colour and surface of the 58 stones removed from different sites of urinary tracts were observed. The largest stone was from bladder weighed 118.5 g. Result showed calcium was present in all the stones. Preponderance of magnesium, ammonium, oxalate and phosphates was also evident in stones from all sites (i.e. kidney, ureter, bladder etc.). Incidence of pure calcium oxalates and calcium phosphate stone was very low. The same was true for the stones having combinations of two constituents (calcium oxalate + calcium phosphate, calcium phosphate + uric acid). Majority of stones had more than three combinations. Ammonium acid urate was present in 86.3 and 97.4% in upper urinary tract and bladder stones, respectively. The quantitative analysis of stone was performed, which revealed that calcium and oxalate was the major constituent of stones irrespective of their sites.

Key words: Urolithiasis, Metabolism, Analysis, Qualitative, Quantitative

INTRODUCTION

Analysis of urinary calculi is an essential step in the examination and initial treatment

* Author for correspondence; E-mail: rathore.daksh@yahoo.com

of the patients with 'Pathari'. Knowledge of the composition of calculi yields fundamental information concerning the pathogenesis of the disease, including metabolic abnormality, presence of infection, possible artifacts and even drug metabolisms. In the report of the patients, physician should note the weight, size and shape of stones, the constituents of the stones and their order of deposition, the presence of a nucleus and its composition, the presence of foreign bodies or artifacts, and the presence and identification of unusual components, such as drugs and drug metabolites. The need for specific analysis increases as progress is made in treating various forms of urothiasis and as inter-relationships among predisposing factor become evident.

Some methods of analyzing the calculi (stones) are I.R. spectroscopy, X-ray diffractions, emissions spectroscopy, chemical methods etc. Keeping in view these facts, the qualitative and quantitative analysis of 58 stones and the urine chemistry of the same patients was carried out.

EXPERIMENTAL

Fifty eight stones were analyzed qualitatively¹ and quantitatively by the method described below. 24 hrs urine samples of the same patients were also collected and analyzed for creatinine, phosphorus, uric acid², citric acid³, magnesium⁴, amino nitrogen⁴, GAGs (Glycosaminoglycans⁵), calcium⁶ and oxalate⁷. Crystalluria was also studied in the urine sample from the same stone formers, at the time of admission, just before operation and after 7 days of operation (Microscopic examination).

Quantitative stone analysis : method

100 mg. of stone powder was treated with 25 mL. of aqua-regia (1 : 3 : HNO₃ : HCl) solution. Heating was done for 1-2 hrs. until 1-2 mL. of residue was left in the beaker. This was dissolved in 100 mL. warm distilled water and filtered. The filtrate was used for the estimation of calcium, magnesium and phosphorus. For oxalate and ammonium estimation, 50 mg. of powdered stone was weighed and sufficient H₂SO₄ was added to give concentration of 5 mg. stone per mL of acid. It was centrifuged and the supernatant was used for the estimation of oxalic acid⁷ and ammonium by Nesslerization.

For uric acid estimation, 25 mg. of powder was mixed with lithium carbonate (4 : 3) and dissolved in warm distilled water. The filtrate was used for the uric acid estimation.

RESULTS AND DISCUSSION

Physical characteristics i.e. the weight, shape, colour and surface of 58 stones removed from different sites of urinary tract are given in Table 1. Weight ranges from 0.05 g. to 0.75 g. The largest stone was from bladder weighing 118.5 g. Mostly the shape of the stones was irregular, colour was generally brown and surface was rough.

Table 1: Physical characteristics of stones

Weight (g)		Renal (20)	Ureteric (16)	Spontaneously voided (10)	Urethral (2)	Unknown (10)
		Mean \pm SD				
Range		1.73 + 1.74	0.54 + 0.47	0.11 + 0.08	0.05 + 0.04	0.62 + 0.39
		0.125 – 6.75	0.05 – 1.5	<0.05 – 0.17	0.05 – 0.17	0.40 – 1.20
Shape (%)	Irregular	65.0	81.20	80.0	100.0	44.4
	Rounded	10.0	-	-	-	-
	Oval	20.0	12.50	-	-	44.4
	Triangular	5.0	6.25	20.0	-	11.1
	Rod shaped	-	-	-	-	-
Colour (%)	White	5.0	18.70	20.0	-	22.2
	Brown	65.0	62.50	60.0	50.0	66.6
	Black/Grey	15.0	6.25	10.0	-	-
	Yellow	15.0	12.50	20.0	50.0	11.1
Surface (%)	Smooth	30.0	25.0	30.0	50.0	33.3
	Rough	65	75.0	70.0	50.0	55.5
	Nodulated	5.0	-	-	-	11.1

The results of the qualitative analysis are presented in Table 2. The results showed 100% prevalence of calcium and phosphate, which is followed by carbonates and oxalate and then magnesium and uric acid. Cystine was absent in all the stones. Occurrence of pure calcium phosphate stone was 36%, calcium phosphate + calcium oxalate stone was 19% and the presence of calcium oxalate + calcium phosphate + uric acid was only 6%. Rest were the mixed types of stones. Table 3 showed the urinary excretion of different parameters in mmol/24 hrs. and quantitative analysis of stones. Quantitatively, oxalate was the major constituent of stones (30.8 + 11.96 mg %). No relationship (r) was observed between 24 hrs.

urine chemistry and stone ingredients. The results of crystalluria (Table-4) revealed that incidence of crystalluria decreased after operations.

Table 2: Qualitative analysis of stones (%)

Radicals	Renal (20)	Ureteric (16)	Spontaneously voided (10)	Urethral (2)	Unknown (10)
Ca ²⁺	100.0	100.0	100.0	100.0	88.8
Mg ²⁺	90.0	37.5	50.0	100.0	88.8
NH ₄ ⁺	100.0	75.0	70.0	100.0	88.8
COO ⁻	90.0	68.7	50.0	100.0	77.7
COO ⁻	90.0	68.7	50.0	100.0	77.7
PO ₄ ³⁻	100.0	100.0	100.0	100.0	100.0
CO ₃ ²⁻	100.0	93.7	90.0	100.0	100.0
Uric acid	25.0	37.5	30.0	100.0	33.3
Cystine	NIL	-	-	-	-

Table 3: Urine chemistry and quantitative analysis of stones

Parameters	Mmol. / 24 hrs. (Mean ± SD)	Quantitative stone analysis (Mg. %)	Correlation coefficient
Creatinine	7.76 + 0.39	-	-
Citric acid	1.63 + 0.42	-	-
Magnesium	2.69 + 0.31	0.80 + 1.96	0.000053 NS
Amino nitrogen	9.87 + 0.53	4.02 + 4.29	-
GAGs**	2.83 + 0.30	-	-
Calcium	4.53 + 0.31	18.10 + 5.71	0.000002 NS
Oxalate	0.47 + 0.02	30.18 + 11.96	- 0.000050 NS
Phosphorus	11.20 + 0.81	3.23 + 4.38	0.000150 NS
Uric acid	1.19 + 0.09	1.44 + 1.84	- 0.000030 NS

* Ammonium

** GAG (Glycosaminoglycans) in CPC Units/24 hrs.

Table 4: Crystalluria (%) in the urine of stone formers

Crystals	At the time of admission	Just before operation	After 7 days of operation
Calcium oxalate			
+4	6.89	6.89	1.72
03	8.60	5.17	5.17
02	34.50	27.58	12.07
01	37.90	34.48	24.14
NIL	12.10	25.86	56.89
Brushite			
+4	-	-	-
+3	5.17	5.17	1.72
+2	17.24	13.79	15.52
+1	31.03	27.58	18.96
NIL	46.55	53.45	63.79
Uric acid			
+4	-	-	-
+3	-	-	-
+2	-	-	-
+1	17.20	18.96	13.79
NIL	82.70	81.03	86.21
Struvite			
+4	-	-	-
+3	8.62	8.62	3.45
+2	20.68	15.52	8.62
+1	39.65	24.14	13.79
NIL	31.03	51.72	74.14

Fifty eight non-infected stone formers were admitted to surgical wards of General Hospital R.N.T., Medical College, Udaipur. Their urine was examined for the crystalluria, at the time of admission, before and after operation and also for 24 hrs. urine chemistry. The

extracted stones from the patients were also analyzed. An excretion of more than 200 mg. calcium per day was present in 37.7% patients. Although not quantitatively analyzed but their calcium intake was not expected to be more than 400-500 mgs./day. This suggests the possibility of the mild absorptive hypercalciuria in these patients. Nevertheless, average calcium excretion was 181.3 ± 94.07 mg/24 hrs. and in this range, it should not pose any risk of stone formation. Because in many populations, the normal calcium excretion remain in between 300 to 400 mg/day^{8,9}.

In recurrent stone formers, the analysis of extracted stones is of utmost important beside other investigations to provide guidelines for appropriate treatment. For example pure uric acid stones call for keeping the urinary pH near neutral or slightly alkaline because it dissolves at high pH. Calcium oxalate and calcium phosphate stone formers should keep their urine more acidic.

Struvites (Magnesium ammonium phosphate) are invariably the results of infection. Ammonium acid urate, a consequence of under nutrition and mixed stones, suggests the intermittent transient precipitation of various factors. The quantitative analysis of stones revealed that oxalate was the most preponderant radical followed by calcium in all types of stones.

This is a common finding in mixed type of stones¹¹. An interesting features was that the oxalic acid content could not be accounted for by the calcium in all the stones suggesting that all the oxalate was not present as calcium oxalate. Although we have not carried out the analysis of other cations except magnesium, which readily forms oxalate salt. Maricker¹⁰ have reported the presence of sodium, potassium, iron chromium, copper, nickel, silver and aluminum. It is quite likely that some of these cations get inter-placed as oxalate salts in matrix. A possibility of direct attachment with matrix also needs to be investigated. Magnesium was present in small proportions, which indicated that the infection was not the major contributor of stone growth. Ammonium acid urate was present in relatively larger quantities in both bladder and kidney stones of patients in all age groups. This is not unexpected also because the infection, excess of acid containing food, starvation, dehydration, inadequate diet, pyrexia (High fever) and infectious diarrhoea are the common problems in local population.

In conclusion salient features of the study are ; (a) presence of calcium and oxalate in all the stones, (b) presence of ammonium in 96.5% of stone, which indicated either presence of struvite or ammonium acid urate and (c) absence of cystine in all the stones.

REFERENCES

1. R. A. Roth and B. Finlayson, *Stones, Clinical Management of Urolithiasis*, Williams and Wilkins, Baltimore/London (1983) p. 82
2. H. Varley, A. H. Gowenlock and M. Bell, *Practical Clinical Biochemistry*, Heinmann Medical Books Ltd., London (1980) p. 196.
3. G. Rajagopal, *Ind. J. Exp. Biol.*, **22**, 391 (1984).
4. S. Natelson, *Techniques of Clinical Chemistry 3rd Ed.* Charles C. Thomas, USA (1971) p. 296, 491 & 576.
5. C. A. Pennock, *J. Clin. Path.*, **29**, 111 (1976).
6. E. M. Gindler and J. D. King, *Am. J. Clin. Path*, **58**, 376 (1972).
7. A. Hodgkinson and A. Williams, *Clin. Chim. Acta.*, **36**, 127 (1972).
8. G. W. Drach, *J. Urol.*, **141(3)**, 711 (1989).
9. J. Lemann and R. W. Gray, *J. Urol.*, **141**, 715 (1989).
10. Y. M. F. Maricker, D. Joseph and P. A. Abraham, *Ind. J. Surg.*, **38(10 & 11)**, 480 (1976).
11. P. Hada, A. K. Pendse, P. P. Singh and P. P. Urolithiosis, *Research Asian Publishing House*, 8/81 Punjabi Bagh, New Delhi (1989) p. 1.
12. M. A. Childs, L. J. Rangel, J. E. Lingeman and A. E. Kranebeck, *Urology.*, **79(5)**, 996 (2012).
13. E. Gnessen, J. A. Mandeville S. E. Handa and J. E. Lingemen, *J. Endo.*, **25(9)**, 1519 (2011).

Accepted : 05.01.2013