

DIFFERENTIAL THERMAL ANALYSIS OF SOME HUMAN STONES

AINUL H. KHAN,* M.A. QAISER and KHURSHID JEHAN*

PCSIR Laboratories, Peshawar

M. KABIR

Department of Surgery, Khyber Medical College, Peshawar

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Abstract. Human stone disease is common in Asiatic countries. Differential thermal analysis of the stones provides a cheap, accurate and simple method of characterization. The DTA curve of whewellite, weddellite, struvite, newberyite, uric acid and cholesetrol stones have been reported.

Human stone disease is endemic in Asiatic countries. It has been a major problem since prehistoric days. McCarrison¹ made extensive studies of the incidence, epidemiology and nutritional aspects of endemic lithiasis in Indo-Pakistan subcontinent. Ahmad² studied the calculus disease of the urinary tract in Pakistan.

A knowledge of the composition of human stones is important because lithiasis is a recurrent disease in many people. Preventive measures are based on such information. Phosphate stones are insoluble in alkaline urine whereas uric acid and cystine stones are relatively soluble. A patient with a particular stone may be treated by changing the pH of his urine. Zinsser *et al.*³ have reported that urinary acidification with chlomerodrin, ammonium chloride or cranberry juice was beneficial in the treatment of struvite stones; but was ineffective for putty-type stones. In a nine-year study with 53 patients cranberry juice (one qt/day) arrested stone formation in 32% of the cases and decreased formation of 60% of the cases. Recently penicillamine and allopurinol have been used for the treatment of cystine and uric acid stones respectively.⁴ Thus there is a great need for accurate identification of calculus.

Earlier methods of identification were based on chemical analysis which identified only radicals. Later on attempts were made to use polarizing microscopes which was very successful method if used by an expert mineralogist. X-ray diffractometry proved to be the most accurate method, but the initial investment (about \$ 75,000) prevented its general use. A method is needed which should be cheap, accurate and simple. The authors have studied the differential thermal characteristics of some of the human stones; and found the method excellent for the identification of calculus.

Differential thermal method was first employed for the identification of minerals by Le Chateliers in 1887. Since then there was a gradual development in instrumentation, and now highly sophisticated DTA apparatus is available in the Western countries.

Experimental

Equipment and Procedure. A simple apparatus costing about \$ 370 has been assembled in these Laboratories.⁶

The sample (—100 mesh sieve) and ignited alumina (inert) are taken in the three holes of a stainless steel crucible and then subjected to a uniform rise of temperature (10°C/min) in a vertical furnace with nichrome wires as heating element. Each hole of the crucible contains 0.3 g material. When the amount of the sample is less than 0.3 g, inert alumina may be incorporated and thoroughly mixed. The furnace temperature is controlled manually by a variable transformer. Chromel-alumel thermocouples (25 gauge) are used for recording temperature. The differential temperature is recorded on an automatic Cambridge recorder having a scale between +1 and -1 mV. The recorder driven by an electrical clock dots every 20 sec on a chart 95 mm wide with a duration of 125 min. For a given thermal reaction the recorder may be made to record either upward or downward from the base line depending on the position of the reacting sample with respect to the beads of the differential thermocouples.

Most of the samples were also studied as a check by X-ray diffractometry, photographs were taken with 114.6 mm dia Debye-Scherrer camera using CuK α radiation.

All the samples were obtained after operating by one of the authors (M.K.) except 8KB which came from Karachi.

Results and Discussion

Kidney Stones. Nine samples of kidney stones were investigated. The results are summarized in Table 1. The two endotherms at about 250 and 880°C are present in all the samples indicating the presence of a common compound whewellite (calcium oxalate monohydrate, CaC₂O₄.H₂O). The samples 2KB and 4KB contain a small endotherm at about 110°C. This endotherm shows the presence of a small amount of weddellite (calcium oxalate dihydrate, CaC₂O₄.2H₂O). The endotherm between 450 and 600°C is present in all the KB samples studied. The mech-

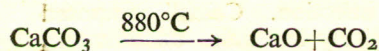
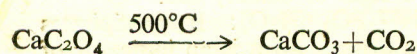
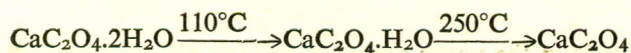
*Now at the PCSIR Laboratories, Karachi

TABLE 1. KIDNEY STONES.

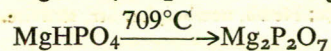
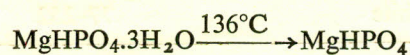
Sample No.	Colour of the stones	Reactions				Inference by	
		Endothermic (°C)		Exothermic (°C)		DTA	X-rays
		Range	Peak	Range	Peak		
1KB	Light yellow	168-288	258			(Wh)	Wh
		773-925	484 883				
2KB	Earthy yellow	72-132	112				
			235	659		High Wh + low wedd	Wh
		495-513	494				
		782-910	889				
3KB	Light brown	190-278	248				
		441-512	488	575		Wh	Wh
		753-906	893				
4KB	Brownish yellow	46-141	104				
		201-259	241			Wh	Wh
		434-509	491			+	
		764-914	897			Wedd	
5KB	Light earthy	160-277	254	492-559	532	Wh	Wh
			437				
			492				
6KB	Earthy yellow	171-273	243	478-543	500	Wh	Wh
			478				
		688-904	885				
7KB	Earthy	103-184	136		447	Wh +	Wh +
		184-302	235		609		
			359	679-729	709	Newb	Newb
		456-507	491				
		729-879	866				
8KB		182-327	242	517-624	587	Wh	Wh
		427-517	494				
		747-909	887				
9KB	Earthy	167-284	250		532	Wh	Wh
		437-500	476				
		707-917	888				

W, whewellite; Wedd, weddellite; Newb, newberyite.

anism of the thermal reactions may be interpreted as follows:



The sample 7KB is rather unique—a mixture of newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$) and whewellite. The endotherm at about 136°C and a small exotherm at about 709°C are indicative of the presence of the former compound. The following reactions may have occurred:



Urinary Bladder Stones. Ten samples of urinary stones were investigated. The differential thermal results are summarized in Table 2.

(i) Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$): Samples 2UB and 3UB contain endotherms at about 250 and 900°C and exotherm about 496°C . Such a curve is characteristic of whewellite.

(ii) Whewellite and Newberyite: The thermogram 4UB is rather complex. The whewellite is easily identified by the endotherms at 240 and 861°C . The endotherm at 127°C seems to be due to the dehydra-

TABLE 2. URINARY BLADDER STONES.

Sample No.	Colour of the stones	Reactions				Inference by	
		Endothermic (°C)		Exothermic (°C)		DTA	X-ray
		Range	Peak	Range	Peak		
1UB	Light yellow	80-104 185-221 340-550	95 205 444	637-816 816-836	806 827	Anhydrous uric acid	U.A.
2UB	Earthy yellow	192-324 456-523 672-921	252 497 906	523-672	651	Whewellite	Wh
3UB	Earthy	68-118 168-290 450-523 732-921	108 250 490 895	523-732	688	Whewellite	Wh
4UB	Light yellow	95-154 197-297 297-380 380-472 472-529 759-877	127 240 361 422 509 861	529-650 650-680	622 662	Whewellite newberyite	Wh+ Newb
5UB	Dirty white	98-206 206-228 228-245 325-370 723-781	150 218 235 351 774	448-518 668-723	478 690	Struvite+ whewellite (trace)	Str + Wh
6UB	Dirty white	109-202 202-359 739-849	159 229 832	429-529 652-739	472 659	Struvite+ whewellite (small amt)	Str + Wh
7UB	Light yellow	86-119 168-219 346-568	104 202 456	619-765 765-820 820-839	750 770 830	Anhydrous uric acid	U.A.
8UB	Yellow	77-95 95-122 335-550	87 104 446	672-887	880	Anhydrous uric acid	U.A.
9UB	Yellow	195-215 342-547	204 447	844-897	874	Anhydrous uric acid	U.A.
10UB	White	77-252	150	647-702	687	Struvite	Str

U.A., uric acid; Wh, whewellite; Newb, newberyite, Str, struvite.

tion of newberyite. This sample is comparable to 7KB. The shift in temperatures is probably due to different proportion of the two compounds.

(iii) Uric Acid ($C_5H_4N_4O_3$): The samples 1UB, 7UB, 8UB and 9UB are mainly composed of uric acid. The diagnostic peak is an endotherm at about 450°C. The exotherms of the four samples are at 827, 830, 880 and 874°C. Such a variation may be the effect of various impurities. Very small endotherms at 100 and 200°C seem to be due to the impurity like whewellite.

Uric acid calculi form in acid urine, and is quite

soluble in the upper ranges of urinary pH.

(iv) Struvite ($MgNH_4PO_4 \cdot 6H_2O$): It precipitates exclusively in alkaline urine. So it is an indicator of alkaline (urea-splitting) infection. Calculi composed of this substance exclusively are quite uncommon.

Struvite calculus is easily recognised by its white to dirty white colour. Sample 10UB is almost pure struvite whereas 5UB and 6UB contain traces of whewellite. Struvite is characterized by a large endotherm at about 150°C and an exotherm at about 690°C. The endotherm seems to be due to the loss of six water molecules. The exotherm may be due to the

TABLE 3. GALL BLADDER STONES.

Sample No.	Colour of the stones	Reactions				Inference by	
		Endothermic (°C)		Exothermic (°C)		DTA	X-rays
		Range	Peak	Range	Peak		
1GB	Yellow	57-123 123-167 507-527	97 156 517			Cholesterol monohydrate	Cholesterol
2GB	Brown	58-113 113-149 366-448	87 137 406	518-618 618-668	568 635	"	—
3GB	Yellow	72-137 137-172 644-737	104 161 714	337-422 470-551	390 521	"	—
4GB	Brownish yellow	67-121 121-160	89 142	512-629	586	"	Cholesterol
5GB	Brownish yellow	65-124 124-170	94 152	492-610 652-705	587 682	"	—
6GB	Brownish yellow	50-104 104-172 744-797	86 149 784	382-457 512-602	412 572	"	—
7GB	Yellow	62-127 127-167 617-745	95 150 722	380-500 517-617	439 564	"	—
8GB	Brown	120-160	147 370 393	470-610 703-770	513 761	"	—

formation of magnesium pyrophosphate from magnesium ammonium phosphate.

Gall-Bladder Stones. Eight samples of gall-bladder stones were analysed by DTA. The results are given in Table 3. All the samples contain two common endotherms at about 100 and 150°C indicating that cholesterol monohydrate ($C_{27}H_{46}O \cdot H_2O$) is the main constituent of the stones. The first endotherm is most probably due to the liberation of water and the second is due to the melting of anhydrous cholesterol.

The thermal behaviour of all the samples at higher temperatures are different. This variation seems to be due to the different amount of impurities which have not been identified.

Other Calculi. The 27 stones studied are largely composed of only six compounds, i.e. whewellite, weddellite, struvite, newberyite, uric acid or cholesterol. Sometimes other compounds such as uric acid dihydrate ($C_5H_4N_4O_3 \cdot 2H_2O$), carbonate apatite $Ca_{10}(PO_4)_6(OH)_2$, brushite ($CaHPO_4 \cdot 2H_2O$), whitlockite ($\beta-Ca_3PO_4$), sodium acid urate ($NaC_5H_3N_4O_3 \cdot H_2O$), ammonium acid urate ($NH_4C_5H_3N_4O_3$), cystine [$-SCH_2CH(NH_2) \cdot COOH$]₂ (250 end; 637 exo.) and

xanthine ($C_5H_4N_4O_2$) (437 end; 724 exo.) may also be present in human stones.

The DTA curves of apatite are generally smooth and featureless,⁷ but may have a minor endothermic peak at about 800°C corresponding to loss of hydroxyl. Urates and brushite were not studied due to the non-availability of the compounds.

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