Thermogravimetric Analysis of Urinary Stones

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Summary—Routine thermogravimetric (TG) analysis of 501 upper urinary calculi from the State of Jammu and Kashmir is described. The technique is simple, rapid and quantitative, and the equipment is easily maintained. The technique was found to be helpful in 95.4% of urinary stones and it is suggested that TG analysis may be employed as a technique of first choice in the routine quantitative analysis of all urinary calculi.

Urolithiasis is a common, recurring disorder and may be linked to certain intrinsic and extrinsic factors in the genesis of urinary calculi (Gray et al., 1982). The composition of such calculi is indicative of metabolic disorders (Modlin and Davies, 1981) and thus of clinical significance, requiring the correct identification of their components (Modlin and Davies, 1981; Gray et al., 1982). Many of these stones are of mixed composition (Murphy and Pyrah, 1962; Modlin and Davies, 1981) and consist of a nucleus surrounded by layers, often marked by differences in colour and composition. The nucleus is, however, indicative of the initial metabolic disorder and determines the treatment to be prescribed.

Chemical analytical methods have the disadvantage of requiring large samples and, at best, indicate only the radicals that are present and not the compounds (Rose and Woodfine, 1976).

Physical methods, such as X-ray crystallography (Sutor and Scheidt, 1968) and infra-red spectroscopy (Modlin and Davies, 1981), will identify the compounds but are not fully quantitative (Rose and Woodfine, 1976).

TG analysis of stones, originally suggested by Strates (1966) and further developed by Strates and Georgacopoulou (1969), Berenyi and Liptay (1971) and Rose and Woodfine (1976), is straightforward, rapid and less expensive than infra-red spectroscopy and X-ray crystallography. It is quantitative, free of radiation, and identifies the compounds in a calculus. Rose and Woodfine (1976) demonstrated a close correlation between the results of a chemical quantitative method and TG analysis of urinary calculi.

The present study describes the routine use of TG analysis of 501 surgically removed upper urinary tract calculi.

Materials and Methods

A total of 501 calculi (445 renal and 56 ureteric) were surgically removed from the upper urinary tract between June 1982 and March 1988. The equipment used for TG analysis was a Stanton Redcroft* TG 760 thermobalance consisting of a microbalance, a balance control module and a twin recorder \( \times 1 \) and \( \times 2 \) to indicate weight and temperature respectively.

The principle of TG analysis is gradually and linearly to heat in a microbalance a small quantity of crushed calculus to a temperature of 1000°C. As the temperature rises, the powder loses weight and the weight changes occurring at particular temperatures are recorded graphically by the twin recorder. These changes are characteristic of the compounds constituting the calculus and indicate their nature and quantity. Details of the procedure have been described by Rose and Woodfine (1976).

* Stanton Redcroft Limited, Cooper Mill Lane, London SW17 0BN.
Each calculus was analysed chemically according to the qualitative method of King and Wooton (1982) and some stones were also analysed by the quantitative method of Varley et al. (1980).

Interior and exterior portions of 50 calcium oxalate calculi (oxalate content > 70%) were subjected to separate TG analysis in order to determine the degree of hydration.

Results

Typical tracings of the various compounds found on TG analysis have been standardised by Rose and Woodfine (1976). TG analysis of 501 upper urinary calculi is shown in the Table.

Of the 50 calcium oxalate stones, the interior and exterior of which were subjected to separate TG analysis, it was found that the content of the interior was 88% monohydrate and 12% dihydrate, whereas the exterior comprised 96% monohydrate and 4% dihydrate.

Discussion

The state of Jammu and Kashmir falls within the “stone belt” of India and upper urinary calculus disease constitutes 35% of the urological workload in this unit; 86.1% of our stones were predominantly calcium oxalate, 81.2% were calcium oxalate monohydrate (whewellite), 4.9% were calcium oxalate dihydrate (weddelite) and 4.9% were a combination of calcium oxalate and calcium phosphate. These figures are higher than those reported in other studies emanating from Western countries (Herring, 1962; Murphy and Pyrah, 1962; Sutor and Wooley, 1972). Of 431 calcium oxalate stones, 339 were found in males and 92 in females. There is a

Table  Thermogravimetric Analysis for 501 Upper Urinary Calculi

<table>
<thead>
<tr>
<th>Constituent compounds</th>
<th>No.</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure calcium oxalate</td>
<td>431</td>
<td>86.1</td>
</tr>
<tr>
<td>Mainly whewellite</td>
<td>406</td>
<td></td>
</tr>
<tr>
<td>Mainly weddelite</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Calcium oxalate/phosphate</td>
<td>25</td>
<td>4.9</td>
</tr>
<tr>
<td>Magnesium ammonium phosphate</td>
<td>14</td>
<td>2.7</td>
</tr>
<tr>
<td>Calcium phosphate</td>
<td>10</td>
<td>1.9</td>
</tr>
<tr>
<td>Uric acid</td>
<td>6</td>
<td>1.2</td>
</tr>
<tr>
<td>Calcium phosphate/magnesium ammonium phosphate</td>
<td>4</td>
<td>0.8</td>
</tr>
<tr>
<td>Calcium oxalate/urate</td>
<td>6</td>
<td>1.2</td>
</tr>
<tr>
<td>Magnesium ammonium phosphate/calcium phosphate</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>Complex mixtures</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>Failures (unidentifiable)</td>
<td>3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

high intake of animal protein in the Kashmir valley and this may be a contributory factor in the high incidence of oxalate stones, although other factors cannot be excluded.

TG analysis is a satisfactory method for the identification of stones composed of pure calcium oxalate and those composed of both calcium oxalate and calcium phosphate (Rose and Woodfine, 1976); the presence of calcium phosphate may be inferred from the reduced oxalate content, correspondingly increased ash and the absence of positive indications of all other compounds.

Opinions differ as to whether calcium oxalate is laid down as monohydrate, dihydrate or both (Jenson, 1940; Prien and Frondel, 1947; Strates, 1966; Elliott, 1973). TG analysis of 50 oxalate stones revealed that monohydrate comprised 88% of the interior and 96% of the exterior. The corresponding dihydrate content was 12% in the interior and 4% in the exterior. Our findings support the observation of Prien and Frondel (1947) that both monohydrate and dihydrate could be precipitated directly from urine on to the stone surface.

TG analysis of magnesium ammonium phosphate presents special problems since the tracing bears some resemblance to that of brushite. In a brushite stone, however, loss of weight occurs at a higher temperature, over a shorter temperature range and is less than that of magnesium ammonium phosphate. In calculi containing both magnesium ammonium phosphate and calcium phosphate, the precise amounts of these 2 compounds cannot be determined by TG analysis and chemical quantitative analysis is required (Varley et al., 1980). For practical purposes, however, it should be remembered that both magnesium ammonium phosphate and calcium phosphate calculi are infective in origin. Of 14 magnesium ammonium phosphate stones, 13 were found in males and only 1 in a female. The reason for the relatively low incidence of magnesium ammonium phosphate stones in this series is not known.

TG identification of uric acid is characteristic. Of 6 uric acid stones, 5 were anhydrous and 1 was hydrated. The latter gave a TG tracing similar to that of ammonium urate and could be distinguished by excluding the presence of ammonia using the chemical method of Varley et al. (1980); 1.2% of our stones were predominantly uric acid, 1.2% uric acid and calcium oxalate and 0.2% were calcium oxalate, calcium phosphate and urate. We found no cystine or xanthine calculi.

Rose and Woodfine (1976) found that TG analysis yielded conclusive information in 63% of their
calculi and was less helpful in a further 31%. We found TG analysis to be conclusive in 83.6% of our calculi and less helpful in the 5.8% which were a combination of magnesium ammonium phosphate and calcium phosphate or other complex mixtures. These required corroboration by the chemical method. TG analysis was unsuccessful in stones which were rich in matrix and cholesterol (0.6%).

The time required for a single TG analysis was approximately 35 min and the amount of material required was very low (10 mg). In cases where TG analysis did not yield a complete result, sufficient material was available for corroboration by the chemical method. TG analysis is free of radiation hazards, quantitative and rapid. The equipment is less costly than that required for X-ray crystallography and infra-red spectroscopy and it is suggested that it could be employed routinely for the quantitative analysis of all urinary calculi.

References


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