Thermochimica Acta, 62 (1983) 149–169
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

RENAL CALCULI ANALYSIS. APPLICATION OF THERMAL ANALYTICAL TECHNIQUES

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(Received 10 August 1982)

ABSTRACT

Quality control carried out in England has shown the very low reliability of the analysis of renal calculi. Many different analytical techniques have been proposed to solve this problem, and are briefly and critically reviewed in this paper. A method based on thermoanalytical techniques is proposed for obtaining reliable results. The pure substances commonly present in the calculi were first characterised by thermal analysis, derivative thermal analysis, and differential thermal analysis. Synthetic mixtures were then analysed as pellets, simulating the composition of the calculi, and finally, natural renal calculi were studied. The calculi were analysed after dissection, examination by stereoscopic microscopy and polarised light being used to identify a possible nucleus which, when present, was isolated and analysed separately.

More than 1000 calculi derived from surgery or from spontaneous emission were analysed. No pretreatment of the calculi is required. The accuracy of the results is about 1.5% and the time required for analysis is about 20 min.

INTRODUCTION

Renal calculi are a symptom and not a pathology, and form because of factors that often manifest themselves intermittently. Nephrolithiasis is a phenomenon that is evidenced only "post facto" after the calculi are present. In the majority of cases, the primary disorder is not known and the urologist must necessarily treat only the symptoms. At present, there is no evidence to support the thesis that calculi of the same composition and crystalline structure have followed a common genetic mechanism.

Once the nucleus is formed, the successive growth of the calculus depends completely on the modifications of the surrounding conditions, that is, the

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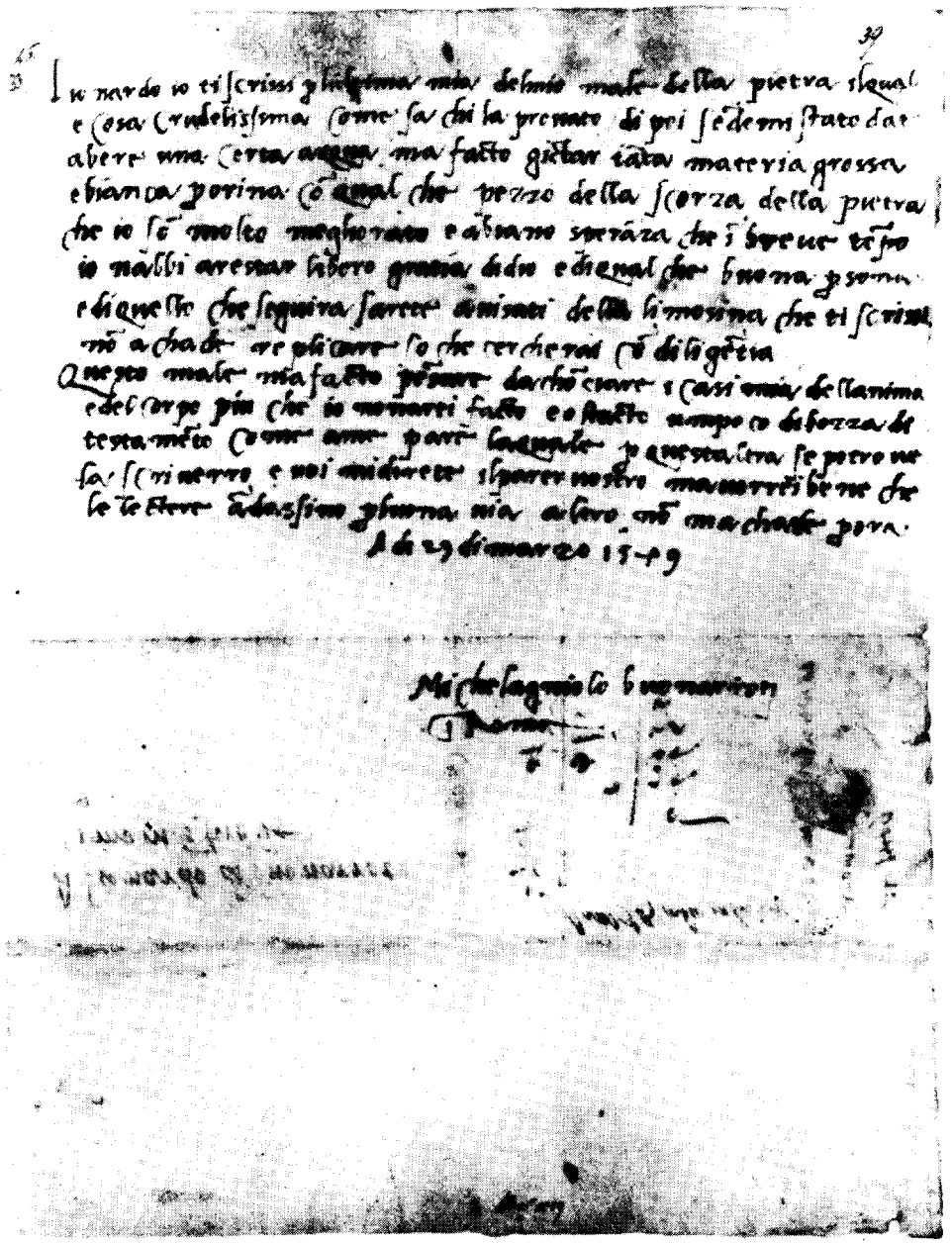

Fig. 1. (British Museum Mil. ccxv From Rome March 23rd 1549.) Lionardo—In my last letter I wrote and told you about my being ill with the stone, which is something cruel, as those who have had it know. Since then, having been given a certain kind of water to drink, it has caused me to discharge so much thick white matter in the urine, together with some fragments of the stone, that I am much better and they hope that in a short time I shall be free of it—thanks to God and to some good soul. As to what ensues you shall be informed. There is no need to repeat what I wrote you about almsgiving. I know that you'll see into it diligently.

This illness has caused me to think more about putting my affairs, both temporal and

chemico-physical modifications of the urine. Nucleation and growth are two completely separate conceptions, especially from an aetiopathological point of view. While the study of nucleation, the primary event, is the major point of interest from the clinical point of view to establish the determining cause of the calculosis, a study of the growth structure produces data concerning the urine modifications that gave rise to the calculus growth. When a nucleus with a chemical composition different from that of the outer shell is present in a calculus, it is possible to suppose that the calculus is an expression of two successive pathological phenomena and it is necessary to intervene on both at a clinical level. Herring [1] and particularly Prien and Prien [2] emphasise this problem. Prien and Prien point out that if the ammonium magnesium phosphate index of a urinary infection is present only in the outer shell of the calculus, it is possible to concede that the infection was not causally correlated with the initial state of formation of the calculus, but developed successively, as a complication, after the central portion, or nucleus, was already present.

In many other cases, it is possible to show nuclei chemically different from the outer shell. These are an indication of a more complex chemical history than is deducible from an undifferentiated analysis.

Commonly, the existence of a nucleus is completely neglected and the analytical datum is referred to in terms of a percentage of the different chemical compounds present in toto in the calculus, independent of their localisation. The pretreatment of the sample generally adopted almost precludes the possibility of discovering the nucleus; the calculus, in fact, is crushed, the powder so obtained is mixed and an average sample is analysed. The consequent impossibility of identifying the existence of a nucleus, e.g. uric acid or cystine, in a calculus of calcium oxalate can lead to the misdirected efforts of the clinician to prevent a recurrence.

Human urinary calculi have been studied by many different workers and by many different techniques. Urolithiasis was already well known in the times of Michelangelo Buonarroti as "mal della pietra" (stone illness), and was treated, as Michelangelo writes (Figs. 1 and 2), by drinking some stone breaking water. Urolithiasis, although with different epidemiologies, is present in almost all human populations and is by now a social illness that requires preventive measures, as well as curatives, that must be based on very reliable data.

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spiritual, in better order than I would have done, and I've sketched out a will that I think suitable, which I'll copy out next time, if I can, and you can give me your opinion. But I should have to make sure the letters were sent by a safe route. I think that's all for the present.

On the 23rd day of March 1549.

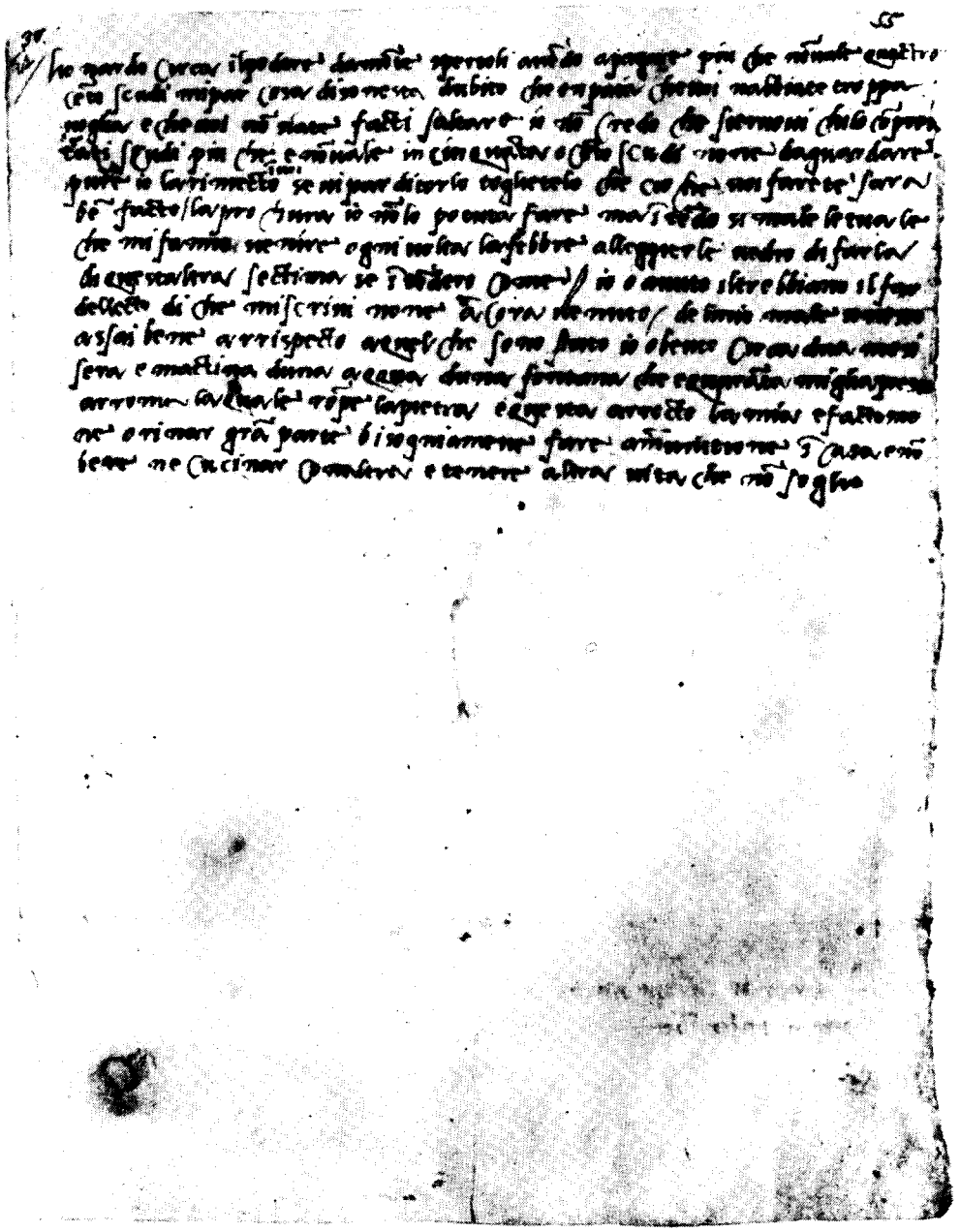

Fig. 2. (British Museum Mil. ccxxiv from Rome June 8th 1549.) Lionardo—As regards the Monte Spertoli farm, if you have to pay four hundred *scudi* more for it than it's worth, it seems to me to be a dishonest deal. I suspect that you seemed too keen and could be made to jump at it. I don't believe there's anyone who'll buy it for so many *scudi* more than it's worth. Within fifty or a hundred *scudi* there's no need to be particular. However, I leave it to you; if you think it advisable to take it, take it, because whatever you do will be satisfactory.

I haven't been able to see to the power of attorney. But I have such difficulty in making

On the other hand, analysis of renal calculi was always considered superficially and quality controls carried out in England by Scott and Barford [2b] have shown the very low reliability of the results.

Analysis of renal calculi has been carried out until recently only by qualitative or semiquantitative techniques, with remarkable errors or considerable interferences. Now, besides chemical analysis, instrumental techniques are used for the analysis of renal calculi, the main ones being:

chemical techniques (at present, some kits for the chemical analysis of the renal calculi are commercially available);

X-ray diffraction and fluorescence;

IR;

polarised light;

thermal analysis.

The chemical techniques, as well as those proposed in the kits, are generally unsatisfactory because:

The low sensitivity of the reactions used makes complete chemical examination impossible for small sized calculi that are often naturally eliminated in the urine and the analysis of which is obviously very important for the prevention of recurrences;

The chemical methods allow identification of radicals but reveal neither how they are arranged in the compounds nor their crystalline structure, which is of great interest for the successive therapeutic treatments.

X-Ray analysis was first applied to the study of renal calculi in 1931 according to Saupe [3] and then from many other workers [4–15]. According to Prien and Prien [2a], who extensively used this technique for the analysis of calculi [7,8], it gives some problems, particularly:

a compound which may be present from 5 to 15% in a mixed sample may remain undiscovered by X-ray diffraction, as corroborated by Lagergren [9];

in a calculus of heterogeneous cross-section, it may be necessary to make a number of separate identifications, each of which will require a "run" of some hours in a conventional X-ray powder camera;

the matrix effect is quite high and the matrix can be quite different;

the analysis requires a long time and the instruments are very expensive.

The IR technique is the most popular instrumental technique for renal

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out your letters that I'm thrown into a fever every time I have to read one. I'll see to it next week—if I can make out what you want.

I've had the *trebbiano*, but the small parcel, about which you write me, hasn't arived yet.

As to my malady, I'm very much better than I have been. Morning and evening for about two months I've been drinking the water from a spring about forty miles from Rome, which breaks up the stone. It has done this for mine and has caused me to discharge a large part of it in the urine. I have had to lay in a supply at home and cannot drink or cook with anything else, and must lead a life to which I am not accustomed.

[*Unsigned*]

analysis and many different papers have been published in this field [16–28]. IR spectroscopy is quite useful for qualitative and quantitative analysis of one-component renal stones, but is found lacking in the quantitative analysis of mixed compounds, and, for example [25], cannot be used to determine small amounts of uric acid if there are aminoacids or if more than 20% oxalate is present in the stone. Care is needed when comparing the spectra of naturally occurring materials, especially mixtures, with the spectra of pure compounds. Minor impurities, particularly in biological materials, may add extraneous absorption bands and slightly change the position, shape or relative intensities of the absorption bands of the major constituents. The detection limits for the various components as referred to by Oliver and Sweet [26] are (as % of total stone): phosphate 1%; oxalate 5%; uric acid/urate 5%; magnesium ammonium phosphate 10% when there are no interferences, but the urate and the oxalate intefere with each other: the principal diagnostic peak for the oxalate at 1300 cm^{-1} is masked by the uric acid absorption in that region and analysis of the oxalate must be carried out by the shoulder at 3400 cm^{-1} that is observable only at oxalate concentrations of 5% or greater.

Most stones contain blood residues that interfere with the detection of magnesium ammonium phosphate and then, considering all these problems, the IR technique is useful, with proper choice of IR library spectra, for qualitative and only semiquantitative analysis of renal calculi.

Few papers concern the use of polarized light in the analysis of renal stones [1,2,7] and basically this technique is useful for qualitative analysis and as an ancillary technique for recognizing the different parts of the calculus to be analyzed, and especially for identification of the nucleus.

The use of thermal analysis in the field of renal calculi was first suggested by Strates in 1966 [30]. Subsequently other authors have applied thermal analytical methods to the analysis of renal stones. The papers of Strates and Georgacopoulou [30,31] represent the embryo of the analytical application of thermal analysis to calculi. In fact, in the first paper Strates refers to only a few data concerning basically calcium oxalate, while in the second one the analysis concerns only a few main components of the most common renal calculi. The Hungarian school of thermal analysis, in cooperation with the Urological Clinic of the Medical University of Budapest, published some papers [32–38] concerning the analysis of renal calculi by thermal methods. The study is particularly interesting, but does not consider some very important problems arising in the field of renal stone analysis, e.g. complex mixtures and the possible interferences deriving from the contemporary presence of different components, problems arising from nucleus identification and its analysis, the importance of which is now well known, and finally the study was carried out only on natural calculi, without any preliminary study on known synthetic mixtures simulating the calculi with the aim of studying the inteference phenomena cited above, and to weight the reliability and confidence of the method.

The most common calculi consist of calcium oxalates, calcium, magnesium and ammonium phosphates, apatites, uric acid and urates, cystine, and mixtures of these compounds, and can include organic substances. Calculi of xanthine are rare. Therefore, the above mentioned compounds were considered in this study.

The calculi of indigo, urostealite and sulphonamide were not examined because they are extremely rare. In order to obtain a highly reliable method for the analysis of renal calculi, we applied thermoanalytical methods, using, in special cases, as ancillary techniques, analysis by stereoscopic and polarising microscopes to identify the nucleus, as well as IR spectroscopy to support qualitative data of possible doubtful interpretation.

The study was carried out characterising the pure substances by thermal analysis (TG), derivative thermal analysis (DTG), and differential thermal analysis (DTA) in an atmosphere of air. Synthetic mixtures (as pellets) with simulated compositions of the calculi were then analysed. Finally, natural renal calculi obtained by the collaboration of the Urologic Clinic of the University of Rome, and the Center for the nephrolithiasis of the Ente Fiuggi, derived ether from surgery or from spontaneous emission were examined. The calculi were analyzed after dissection, examination by stereoscopic microscopy and polarized light to identify a possible nucleus which, when present, was isolated and analyzed separately.

EXPERIMENTAL

Apparatus and reagents

TG, DTG and DTA curves were obtained using a 990 DuPont instrument with a DTA furnace useful till 1200°C and a 951 DuPont thermobalance. The temperature increase was 10°C min^{-1}. The samples ranged between 1 and 10 mg. The furnace atmosphere was air previously dried by bubbling in concentrated sulphuric acid, and the gas flow was 50–100 ml min^{-1}. All the temperatures were corrected for the nonlinear response of the thermocouples and are, of course, the procedural temperatures pdts. All the reagents used were supplied by Merck.

Thermal analysis, TG, DTG and DTA of the pure substances commonly present in the renal calculi were first carried out, the curves of which are reproduced in Figs. 3–13, respectively. The curves of the pure substances allow identification of the processes corresponding to each transformation induced by the temperature, and constitute, if obtained in the same conditions, the standard curves against which the examined samples can be compared.

To check the reliability of the proposed method, pure substances, synthetic mixtures, suitably homogenized, simulating the composition of the

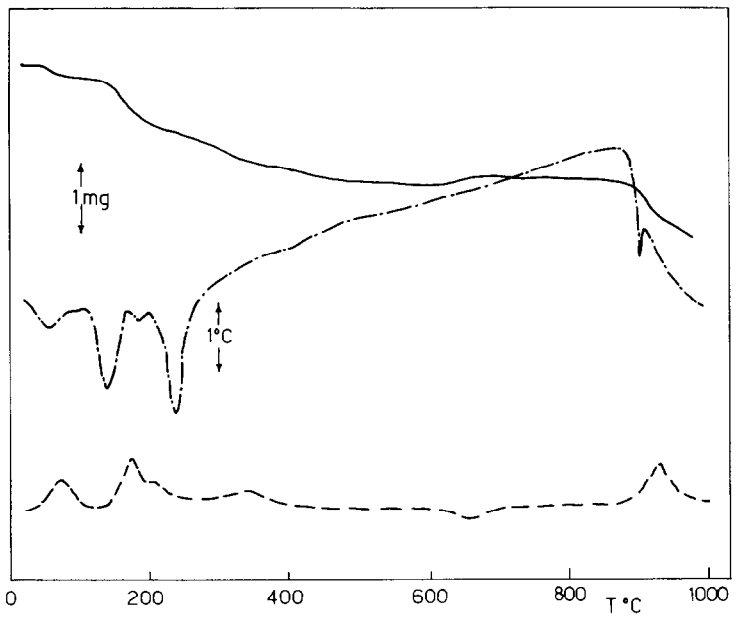

Fig. 3. Calcium bis(dihydrogenphosphate)monohydrate. ————, TG; — — —, DTG; and ·—·—·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

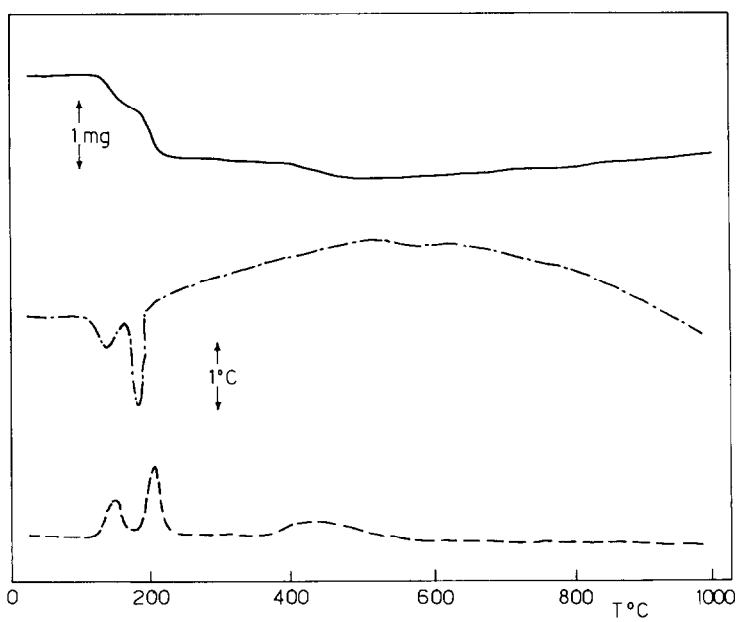

Fig. 4. Calcium hydrogenphosphate dihydrate. ————, TG, — — —, DTG; and ·—·—·, DTA, curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

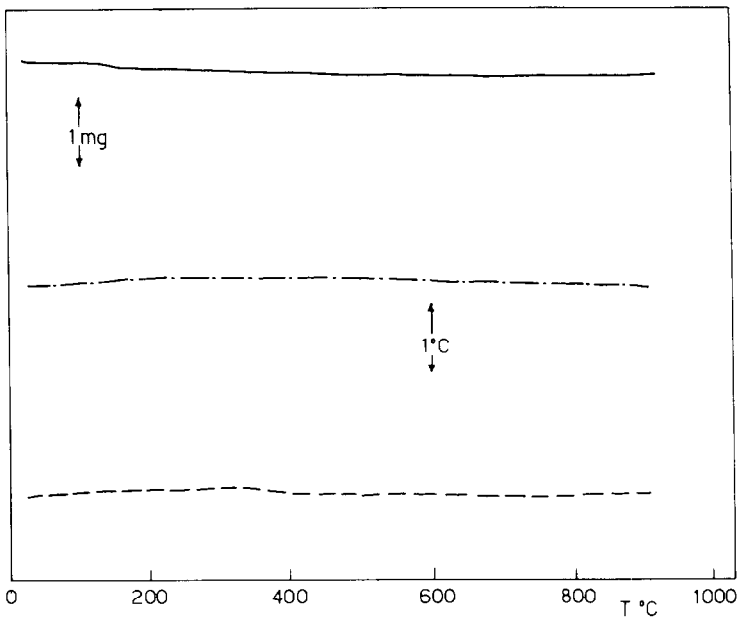

Fig. 5. Apatite. ————, TG; — — —, DTG; and ·–·–·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

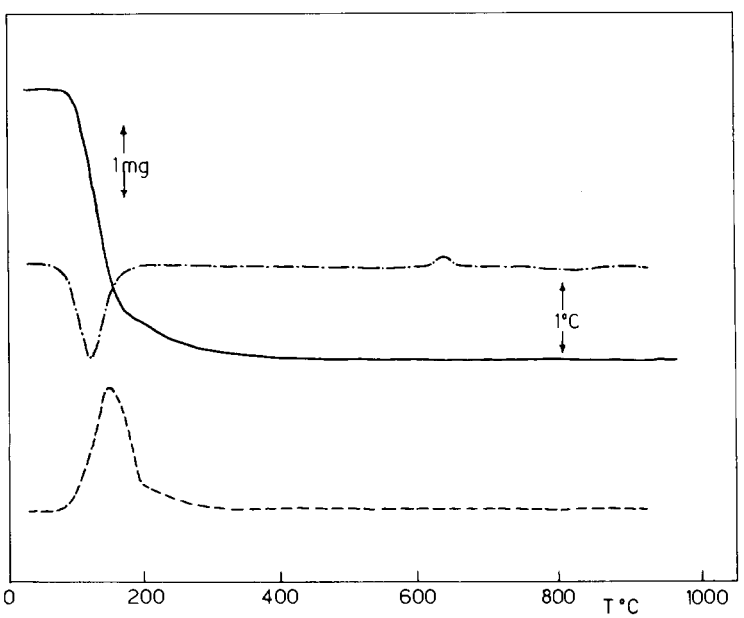

Fig. 6. Ammonium magnesium phosphate hexahydrate. ————, TG; — — —, DTG; and ·–·–·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

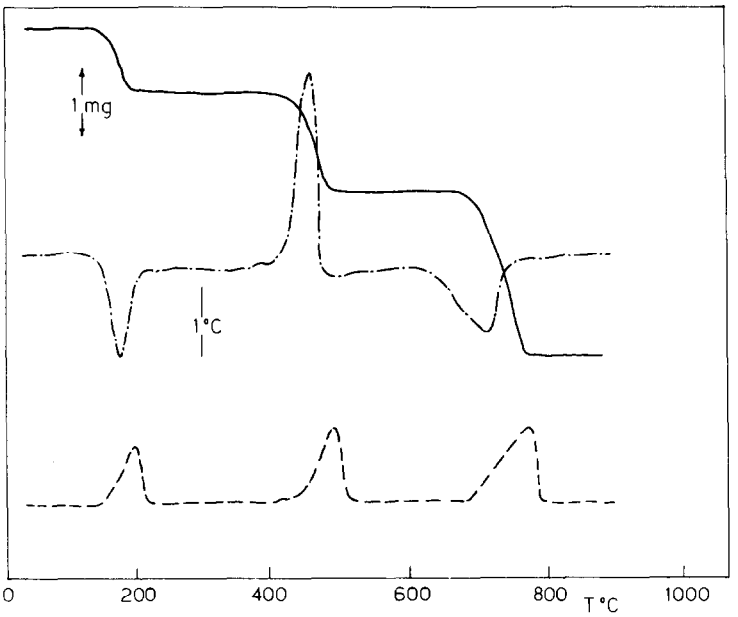

Fig. 7. Calcium oxalate monohydrate. ————, TG; — — —, DTG; and ·-·-·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

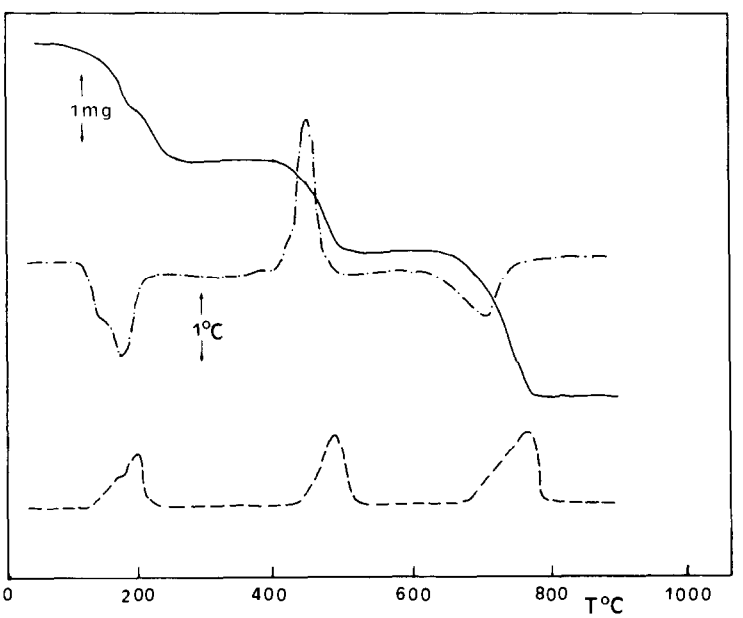

Fig. 8. Calcium oxalate dihydrate. ————, TG; — — —DTG; and ·-·-·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

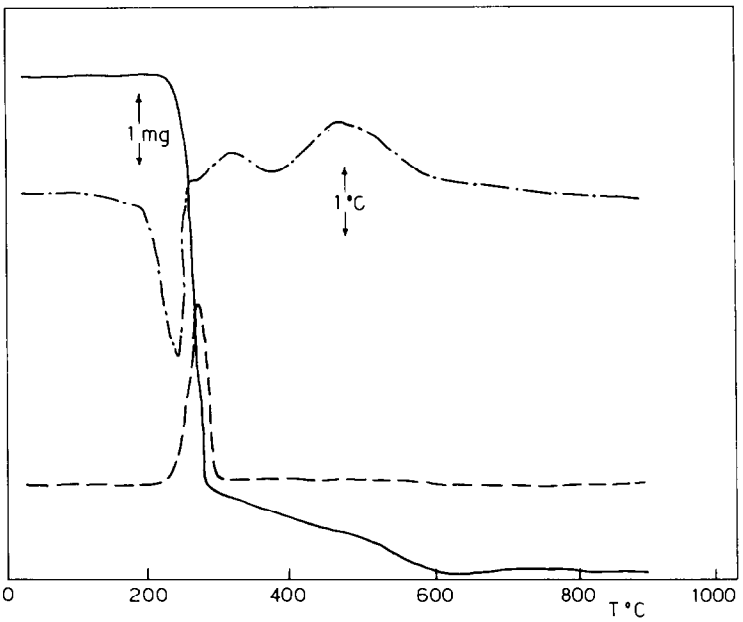

Fig. 9. Cystin. ————, TG; — — —, DTG; and ·-·-·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

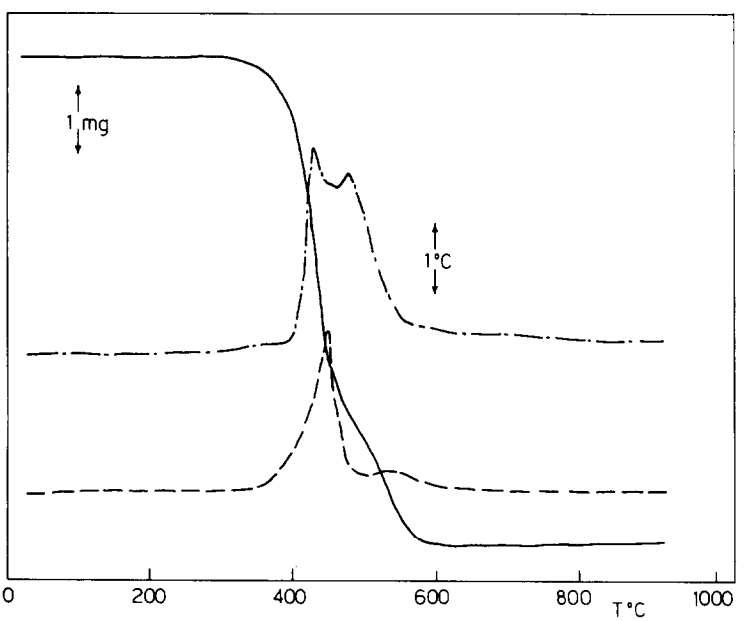

Fig. 10. Xanthyn. ————, TG; — — —, DTG; and ·-·-·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

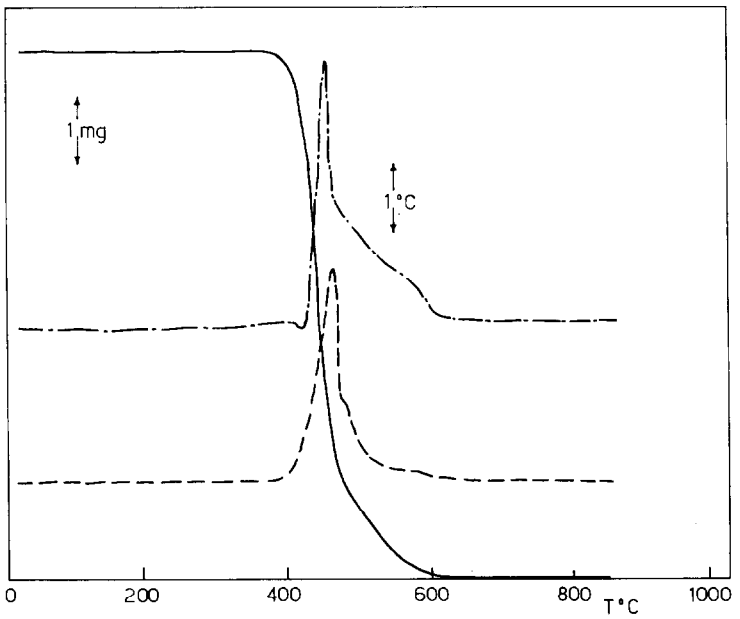

Fig. 11. Uric acid. ————, TG; — — —, DTG; and ·–·–·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

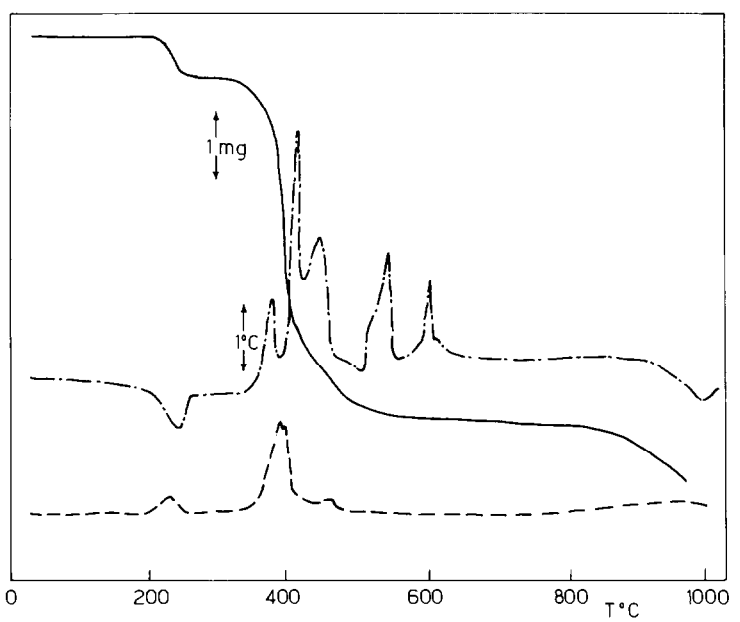

Fig. 12. Monosodic salt of uric acid (monohydrate). ————, TG; — — —, DTG; and ·–·–·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

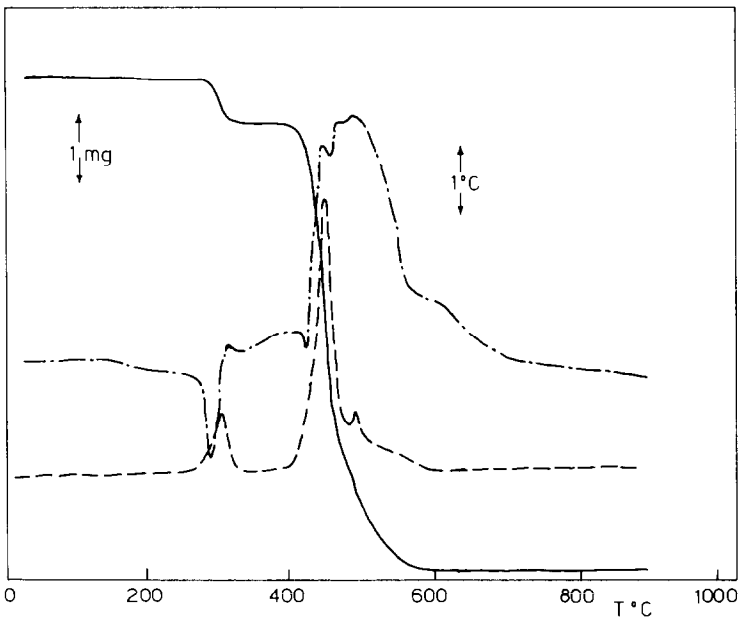

Fig. 13. Monoammonic salt of uric acid. ————, TG; — — —, DTG; and ·-·-·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

calculi composed of two or more components (in calculi, it is very difficult for more than three components to be present in addition to the included organic substances) were prepared by weighing. Qualitative analysis was carried out by comparing the TG, DTG and DTA curves of the unknown samples with those of the pure substances and recognising the components of the unknown samples by the DTA and DTG peaks and by TG steps peculiar to the standards.

Quantitative analysis was carried out using the TG curves, which show the weight changes concerning each step of the curve. To each weight change corresponds a decomposition reaction, the stoichiometry of which is known from the TG curves obtained for the pure substances, and this allows calculation of the amount of compound in the mixture. Sometimes, decomposition phenomena concerning different substances may fall very close to or in the same temperature range, so that the TG steps corresponding to the examined substances overlap, giving only one step on the curve. In this case, it is necessary to set a system of as many equations as there are components of the sample shown by qualitative analysis, where the known parameters are the values of the heights of the TG steps. The TG, DTG and DTA curves corresponding to a mixture of calcium oxalate monohydrate and uric acid, where the percentages of the two compounds are 49.30% and 50.70%, respectively, are collected in Fig. 14.

Qualitative analysis is obtained by comparing the TG, DTG and DTA curves of the synthetic mixture with those of the single pure substances. The

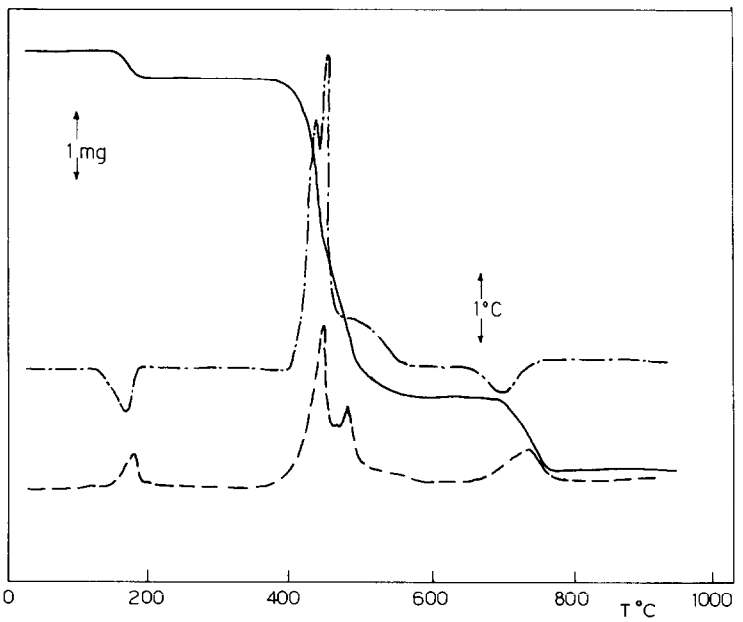

Fig. 14. Synthetic mixture of calcium oxalate monohydrate (49.3%) and uric acid (50.7%). ————, TG; — — —, DTG; and · - · - ·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

TG curve of the mixture shows three steps, the second of which is doubled because of two overlapping processes, localised in the temperature ranges 150–200°C, 375–570°C, and 680–765°C, respectively. To those steps correspond, respectively, on the DTG curve a maximum at 180°C, two maxima corresponding to two overlapping processes at 445 and 485°C, and finally a maximum at 745°C.

On the DTA curve of the synthetic mixture, it is possible to identify first an endothermic peak with a minimum at 170°C, followed by two exothermic peaks, not completely resolved, the maxima of which are localised at 445 and 465°C, followed by a shoulder between 470 and 555°C; finally, there is an endothermic peak with a minimum at 685°C.

Looking now at the TG, DTG and DTA curves of the calcium oxalate monohydrate, it is possible to see that the TG curve shows three steps localised in the temperature ranges 150–200°C, 395–500°C and 670–765°C, respectively, which correspond on the DTG curve to three maxima at 185, 480 and 745°C, and on the DTA curve a minimum corresponding to an endothermic process at 185°C, a maximum corresponding to an exothermic process at 465°C, and finally a minimum corresponding to an endothermic process at 715°C.

Some processes of the TG, DTG and DTA curves of the mixtures can be found on the curves obtained for calcium oxalate monohydrate while others,

the DTG maximum at 445°C, the DTA maximum at 445°C, and the doubling of the second TG step, cannot be found on the same curves.

Examining the curves corresponding to uric acid, it is possible to see that the TG curve shows only one step in the range 380–590°C, concerning the decomposition, which corresponds to a maximum at 445°C on the DTG curve. The DTA curve shows first a small endothermic process with a minimum at 415°C, corresponding to the start of the demolition of the crystalline structure which immediately follows an exothermic asymmetrical process with a maximum at 445°C, corresponding to oxidative decomposition of the molecule.

The TG curve step and the maximum at 445°C of the DTG curve of uric acid justify the doubling of the second step and the presence of the maximum at 445°C on the TG and DTG curves of the mixture, respectively. It is interesting to note that when calcium oxalate predominates in the mixture, the small endothermic peak of uric acid tends to disappear (Fig. 12). On the other hand, where uric acid predominates, the exothermic phenomenon corresponding to the oxidative demolition of the uric acid covers that corresponding to the decomposition reaction of the oxalate that shows itself as a shoulder on the curve.

Quantitative analysis is obtained by the TG curves when the unknown components are identified. In the examined case, the first step of the TG curve of the mixture corresponds to the dehydration reaction of calcium oxalate monohydrate

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O \tag{1}$$

The second step corresponds instead to the summation of two processes

$$CaC_2O_4 \rightarrow CaCO_3 + CO \tag{2}$$

total decomposition of the uric acid without any residue (3)

and the third step corresponds to the reaction

$$CaCO_3 \rightarrow CaO + CO_2 \tag{4}$$

the residue is composed of calcium oxide. If the weight loss corresponding to each step, or the weight of the residue and the reactions associated with the weight losses are known, it is possible to set a system of equations allowing the weight of each component of the mixture to be obtained. In the examined case, the number of components of the mixture being two, a system of two equations is sufficient; therefore, considering the second and the third TG steps

$$W_2 = x\frac{CO}{CaC_2O_4 \cdot H_2O} + y$$

where x is the weight of calcium oxalate monohydrate in the mixture, y is the weight of uric acid in the mixture, and $CO/CaC_2O_4 \cdot H_2O$ is the % weight loss corresponding to reaction (2).

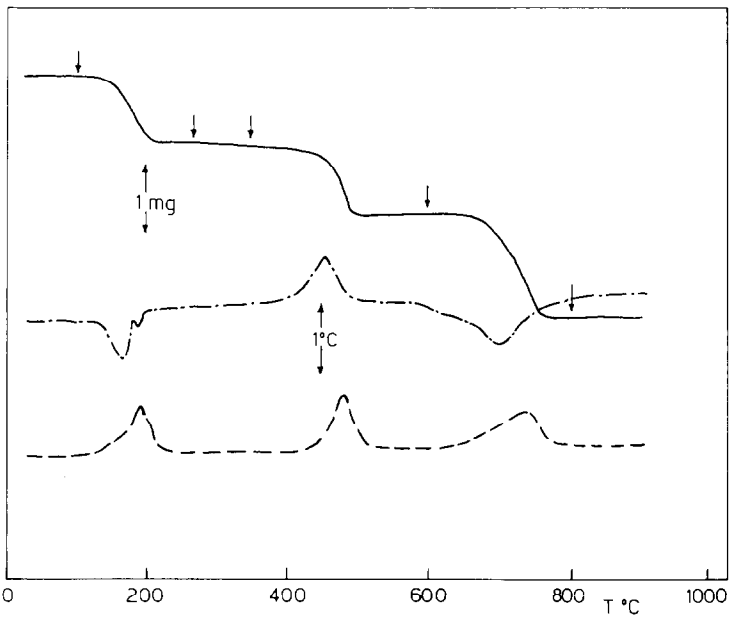

Fig. 15. Synthetic mixture of calcium oxalate monohydrate (68.3%) and calcium hydrogenphosphate dihydrate (31.7%). ————, TG; — — —, DTG; and ·–·–·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

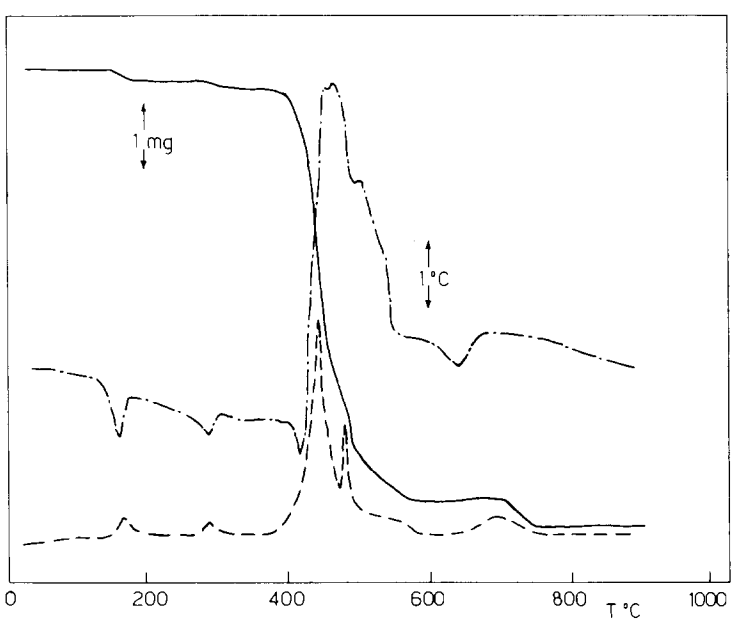

Fig. 16. Synthetic mixture of calcium oxalate monohydrate (23.1%), uric acid (56.0%) and the monoammonic salt of uric acid (20.9%). ————, TG; — — —, DTG; and ·–·–·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

In the case of uric acid the weight loss corresponds to 100% of the acid in the mixture because this decomposes to give totally gaseous products, and then the coefficient by which y must be multiplied is 1.

$$W_3 = x \frac{CO_2}{CaC_2O_4 \cdot H_2O}$$

where $CO_2/CaC_2O_4 \cdot H_2O$ is the % weight loss corresponding to reaction (4).

As in the second equation, it would have been possible to use that obtainable by the first step or that obtainable by the residue.

As an example, Figs. 15 and 16 show the TG, DTG and DTA curves corresponding to two synthetic mixtures. The arrows indicate the points where the weight variations were measured.

The TG, DTG and DTA curves corresponding to natural calculi are shown in Figs. 17–19.

Examining Fig. 15, it is possible to see that in the temperature range 220–520°C the TG curve shows a weight loss which is not present on the curve corresponding to the synthetic mixture composed of the same components referred to in Fig. 15. On the DTA curve an exothermic phenomenon corresponds to this weight loss. This behaviour can be assigned to the degradation of organic substances which may be present in the calculi.

Finally the influence of the speed of the temperature increase was studied and it was found that by increasing this parameter a sharp improvement of

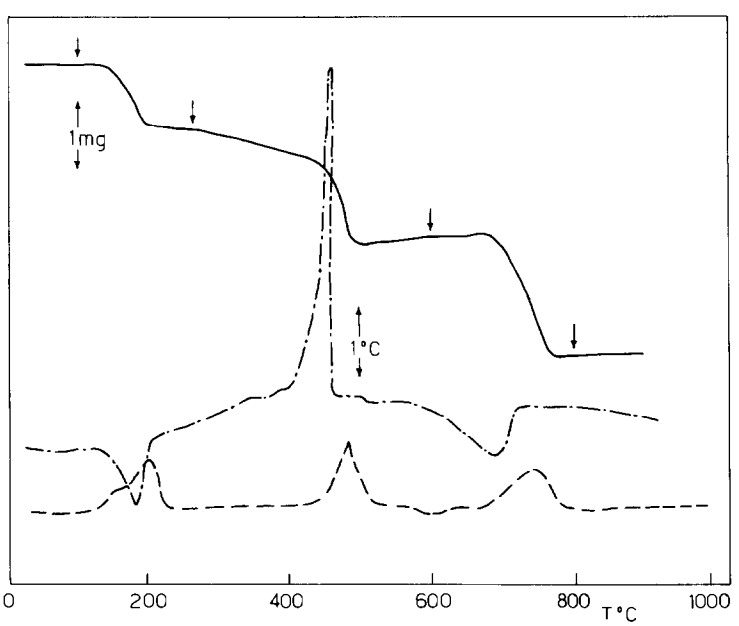

Fig. 17. Calculus of composition: calcium oxalate monohydrate 79%, calcium hydrogenphosphate dihydrate 16%, and organic substances 5%. ————, TG; — — —, DTG; and ·–·–·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

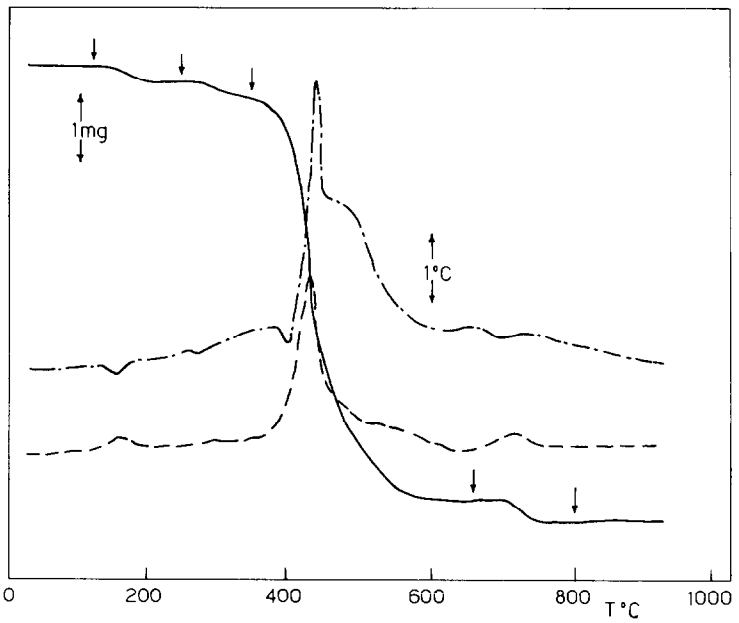

Fig. 18. Calculus of composition: calcium oxalate monohydrate 19%, the monoammonic salt of uric acid 21%, and uric acid 60%. ————, TG; — — —, DTG; and · - · - ·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

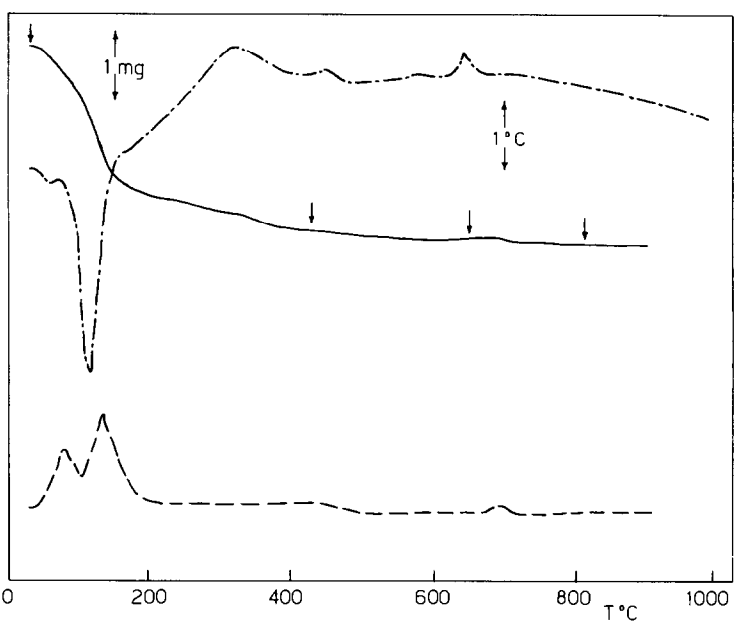

Fig. 19. Calculus of composition: calcium oxalate monohydrate 4%, ammonium magnesium phosphate hexahydrate 75%, and apatite 21%. ————, TG; — — —, DTG; and · - · - ·, DTA curves. Heating rate: 10°C min^{-1}. Atmosphere: air.

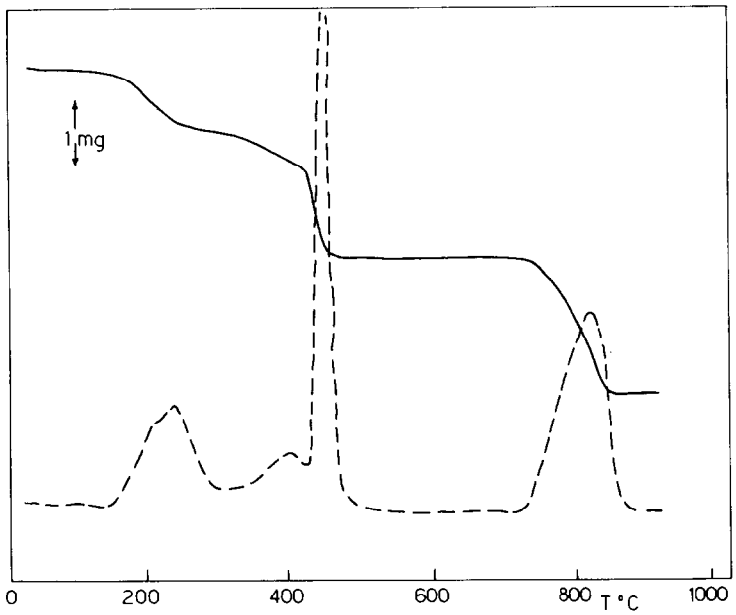

Fig. 20. Nucleus of a calculus. Composition: calcium oxalate monohydrate 95%, and uric acid 5%. ————, TG; and — — —, DTG curves. Heating rate: 50°C min^{-1}. Atmosphere: air.

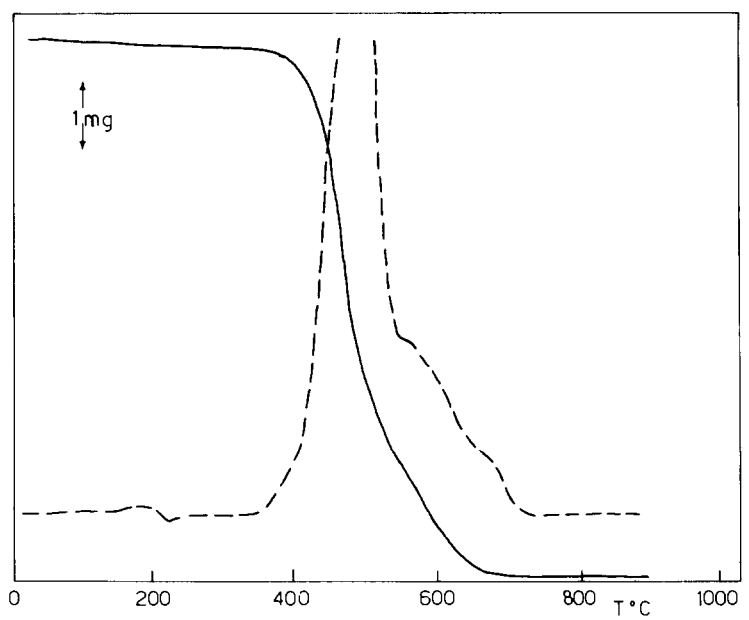

Fig. 21. Outer shell of the calculus of Fig. 20. Composition: uric acid 100%. ————, TG; and — — —, DTG curves. Heating rate: 50°C min^{-1}. Atmosphere: air.

the behaviour of the DTG curve was obtained, with better separation and evidence of the processes, while the TG curve remains perfectly defined and useful quantitatively, as shown by Figs. 20 and 21 corresponding to the TG and DTG analysis of the nucleus and the external layer of the corresponding calculus. It is interesting to note in this particular case that the nucleus is composed mainly of calcium oxalate monohydrate, while the external layer is composed exclusively of uric acid. The enhancement of the speed of the temperature increase gives another advantage, that is, a reduction in analysis times.

DISCUSSION

Thermoanalytical techniques are a tool of high potential in the field of nephrolithiasis, allowing the realisation of an analytical method useful not only in obtaining the qualitative and quantitative analysis of the chemical species present in the calculus, but also in determining the crystalline structure of the chemical species present in the calculi, knowledge which is fundamental for a correct therapeutical treatment, or the hydration state of the salts that constitute the nephrolites.

The proposed analytical method allows the realisation of the analysis of a calculus, especially using high speeds of temperature increase, in very short times, also useful for routine purposes. The method identifies the possible nucleus, does not require sample pretreatment, is simple, and has an accuracy of about 1.5%. Only in the case of extremely complex, and then very rare calculi, are interferences possible. In such a case, it is useful to realise the analysis by a comparative method using other analytical techniques.

Finally, it is possible to couple the thermoanalytical instrumentation with a computer, and thus, using appropriate programs, obtain direct processing of the instrumental signals, and so obtain the analytical data immediately. More than 1000 calculi were analysed by this method, and a previous statistical treatment of the obtained data are collected in a communication at the XVIII Congress of the International Society of Urology [39].

ACKNOWLEDGEMENT

This work was supported by the National Research Council (C.N.R.).

REFERENCES

1 L.C. Herring, J. Urol., 88 (1962) 545.
2 (a) L.E. Prien and L.E. Prien, Jr., Am. J. Med., 45 (1968) 654.

(b) P. Scott and D.J. Barford, 10th International Congress of Clinical Chemistry, Mexico City, 1978, Abstracts Book No. 310, p. 135.
3 E. Saupe, Fortschr. Geb. Röntgenstr., 44 (1931) 204.
4 A. Tovberg Jensen and J.E. Thygesen, Z. Urol., 32 (1938) 659.
5 A. Tovberg Jensen, Acta Chir. Scand., 84 (1940) 217.
6 A. Tovberg Jensen, Acta Chir. Scand., 85 (1941) 473.
7 E.L. Prien and C. Frondel, J. Urol., 57 (1947) 949.
8 E.L. Prien, J. Urol., 89 (1963) 917.
9 C. Lagergren, Acta Radiol., Suppl., 133 (1956) 1.
10 K. Lonsdale and D.J. Sutor, Science, 154 (1966) 1353.
11 J.D. Sutor and S. Scheidt, Br. J. Urol., 40 (1968) 22.
12 J.D. Sutor, Br. J. Urol., 40 (1968) 29.
13 K.R. MacKenzie and R. Wilson, Br. J. Urol., 43 (1971) 149.
14 R. Mongiorgi, J. Clin. Med., 52 (1971) 681.
15 H.J. Hiralal, Indian J. Pure Appl. Phys., 17 (1979) 241.
16 D.E. Beischer, J. Urol., 73 (1955) 653.
17 G. Chihara, N. Kurosawa and E. Takasaki, Chem. Pharm. Bull. (Tokyo), 7 (1959) 622.
18 M. Weissman, B. Klein and J. Berkowitz, Anal. Chem., 31 (1959) 1334.
19 J. Yean-Chin, J. Urol., 86 (1961) 838.
20 S.S. Pollack and G.L. Carlson, Am. J. Clin. Pathol., 52 (1969) 656.
21 P. Haux and S. Natelson, Microchem. J., 15 (1970) 126.
22 H. Fryett and P. Chan, Invest. Urol., 10 (1972) 144.
23 M.D. Navarro, and B.Q. Guevara, Acta Manilana, Ser. A, 10 (1973) 3.
24 A. Hesse, H.J. Schneider and E. Hienzch, Jena Rev., 18 (1973) 282.
25 R.W. Hannah, Lab. Med. Newsl., 5 (1973) 1.
26 L.K. Oliver and R.V. Sweet, Clin. Chim. Acta, 72 (1976) 17.
27 A. Ligabue and R. Biagi, Quad. Sclavo Diagn. Clin. Lab., 12 (1976) 501.
28 C. Laurence, D. Dubreil and P. Lustenberger, Ann. Chim., (1976) 55.
29 A. Ligabue, R. Biagi, M. Fini and G. Bertusi, Quad. Sclavo Diagn. Clin. Lab., 13 (1977) 186.
30 B.S. Strates, Experientia, 22 (1966) 574.
31 B.S. Strates and C. Georgacopoulou, 15 (1969) 304.
32 G. Liptay, M. Bereney, L. Erdey and A. Babics, Orv. Hetil., 107 (1966) 155.
33 G. Liptay and M. Bereney, VIth International Congress of Clinical Chemistry, Abstracts S. Karger, 1966.
34 M. Bereney, G. Liptay, A. Babics and L. Erdey, Z. Urol., 60 (1967) 361.
35 G. Liptay and M. Bereney, Z. Klin. Chem. Klin. Biochem., 5 (1967) 188.
36 M. Bereney, G. Liptay and A. Babics, Z. Urol., 61 (1968) 209.
37 M. Bereney and G. Liptay, J. Therm. Anal., 3 (1971) 437.
38 M. Bereney, Int. Symp. Renal Stone Res., Madrid, 1972, Karger, Basel 1973, pp. 209–212.
39 M. Pavone-Macaluso and L. Miano, Proceeding of the 18th Congress of the International Society of Urology, Paris, 24–29 June 1979, p. 113.