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THE USE OF THERMAL ANALYSIS IN DETERMINATION OF SOME URINARY CALCULI OF CALCIUM OXALATE

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Abstract

The human urinary calculi are mainly constituted by calcium oxalate, magnesium ammonium phosphate hexahydrate, and uric acid. The ions or molecules are easily characterized by wet chemical methods. The difficulties appear in the differentiation of the hydrates of calcium oxalate (monohydrate COM or Whewellite, and dihydrate COD or Weddelite). A high level of COD in the urinary stones leads, often, inflammation, sharp pain and blood in urine. In the worse cases, they must be extracted by surgical way.

The identification of the main components of urinary calculi, the knowledge of the true number of water molecules bounded to the calcium oxalate, and the determination of each hydrate in the mixture, are the interests of this memory. The thermal analysis (simultaneous DTA-TG) was applied on thirty-three urinary calculi. The determination of the calcium oxalate hydrates was confirmed by calorimetry (DSC).

Keywords: calcium oxalate, DSC, DTA, magnesium ammonium phosphate, TG, uric acid, Weddelite, Whewellite

Introduction

Human renal calculi are coming from a biological maladjustment of the urine. The stone is attributed to the supersaturation of the urine and to the retention of solid particles. It is spreading by successive aggregations and crystal growths. Its composition can be homogeneous, from the nucleous to the periphery, but also, very often, heterogeneous [1, 2]. In the USA, a statistical analysis, done on 10 000 urinary calculi, showed the following distribution [3], with respect to the major component at more than 50%: calcium oxalate, 73.1% (with 31.7% of monohydrate and 41.4% of dihydrate), phosphate 17.5% (with 9.22% of magnesium ammonium phosphate

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hexahydrate), uric acid and urates 7.63% (with 7.48% of uric acid). A study executed on the contemporary patient's and with those of last-century patients, showed differences which can be hypothetically ascribed to the patient's different diets and countries [4]. The presence of the calcium oxalate can be explained by a diet based on vegetables (i.e. beetroots, carrots, celeries, tomatoes, spinachs), fruits (oranges, raspberries, strawberries), potions (coffee, tea), chocolate. Urates are present in meat, fish, but also in some legums (lentils, kidney-beans). The influence of genetic factor must, also, be considered [4].

The calcium oxalate monohydrate (COM) stone is evacuated two times more frequently, than the calcium oxalate dihydrate one. The calcium oxalate dihydrate (COD) is formed by sharp crystals, leading to complications, with the presence of blood in urine. It must be extracted by surgical way in the worse cases. The COD is calcium-dependent, on the contrary, the COM is oxalate-dependent [1].

Chemical characterization of ions and molecules is easy: calcium, magnesium, ammonium, phosphate, carbonate, oxalate, oxalic acid,…[5]. In France, chemical composition of the stone is the only information usually given by the biologist to the clinician [6]. In order to give the maximum of informations, it is necessary to use some others technics: IR spectroscopy, widely used [7–10], Raman spectroscopy [11], X-ray diffraction [12], NMR method [13].

Another way, thermal analysis [14]: differential thermal analysis (DTA), thermogravimetry (TG), differential scanning calorimetry (DSC), can, also, characterize the main components (alone or in mixture) in urinary calculi: calcium oxalate dihydrate (COD) or Weddelite, calcium oxalate monohydrate (COM) or Whewellite, magnesium ammonium phosphate hexahydrate (MAPH) or struvite, and uric acid (UA) or uricite.

The goal of this study was, first, to differentiate, by thermal analysis, the molecular forms in the renal calculi: COM, COD, MAPH, UA; and then, to determine the level of COM and mainly COD, in the calculi containing these two forms. We have considered the calcium oxalate hydrate as the formula $Ca(COO)_2{\cdot}xH_2O$ with x corresponding to the number of bounded water (x is between 1 and 2). The trihydrate isomer exists, but is very rare.

Materials and methods

Samples

The following standards were used: COM from Prolabo (Fontenay-Sous-Bois, France) and Carlo Erba Reactifs (Nanterre, France), UA from Prolabo (Fontenay-Sous-Bois, France) and Fisher Scientific Osi (Elancourt, France). The MAPH was prepared in our laboratory. Pure Weddelite (COD) is somewhat difficult to prepare and on heating, both Weddelite and Whewellite decompose to anhydrous calcium oxalate, which can rehydrate, during, or after cooling down, but only to the monohydrate form [15].

First, the identification of each studied stone was done, by wet chemical way [5] and infrared spectroscopy [16]. The COM and the COD presented the same bands:

broad at about 2900–3400 and 1600 cm^{-1}, sharp at 1300 cm^{-1}. The COM presented a band at 650 cm^{-1}. In addition, the band at 770 cm^{-1} is sharp for the COM, in opposite, broad and rounded for the COD [15]. X-ray diffraction was done on two urinary calculi: the first, as COM, and the second, as COD. The characterization was made [12] by R. Boistelle (CRMC2–CNRS–Marseille–Luminy). Powdered urinary calculi were characterized by the thermal methods.

Thermal analysis procedure

A simultaneous thermal analysis apparatus (TG-DTA Setaram 92) was used, with: heating rate 5°C min^{-1}, from the ambient temperature to 850°C, gas sweeping: air (0.5 L h^{-1}) or nitrogen (2.5 L h^{-1}). Thermocouples and crucibles were platinum. The sample mass was 10 mg, and kaolin was used as an inert thermal reference.

A DSC apparatus (Setaram 92) was, also, used, with a heating rate of 0.3°C min^{-1}, between 100 to 180°C. The opened crucibles were aluminium of 100 μL capacity. Sample was 10 mg, and the inert standard, kaolin. Indium, tin, lead and aluminium were used as standards of temperature and enthalpy's determinations.

Unfortunately, urinary calculi were obtained without acknowledgement of their source or of the patient history for each. So, we have no way to judge the calculi composition based upon the disease etiology from which the stones were derived. But, all the analysed urinary calculi were formed in the kidneys, and/or in the urinary tract.

Experimental

First, we show the characterization of each component, and then, the quantitative determination of COM and COD in mixture.

Qualitative analysis

Calcium oxalate monohydrate (COM)

Under nitrogen sweeping, the TG, DTG (derivative curve of the thermogravimetry) and DTA curves of the COM standard, display three typical steps, located in the temperature ranges of about 100–220, 450–520 and 600–800°C [17, 18]:

$$1^{st}\text{ step } CaC_2O_4{\cdot}H_2O \rightarrow CaC_2O_4+H_2O$$

$$2^{nd}\text{ step } CaC_2O_4 \rightarrow CaCO_3+CO$$

$$3^{rd}\text{ step } CaCO_3 \rightarrow CaO+CO_2$$

Under air sweeping, the carbon monoxide is oxidized into carbon dioxide, so, an exothermic peak appears in the 2nd step (Fig. 1). The observed curves, run on a urinary stone (Fig. 2), are near those of the pure COM, with a light difference at about 348°C, the presence of a broad and small exothermic peak is attributed to the non-crystalline organic compounds oxidation (globulines, cellular chips,…) present in urinary calculi.

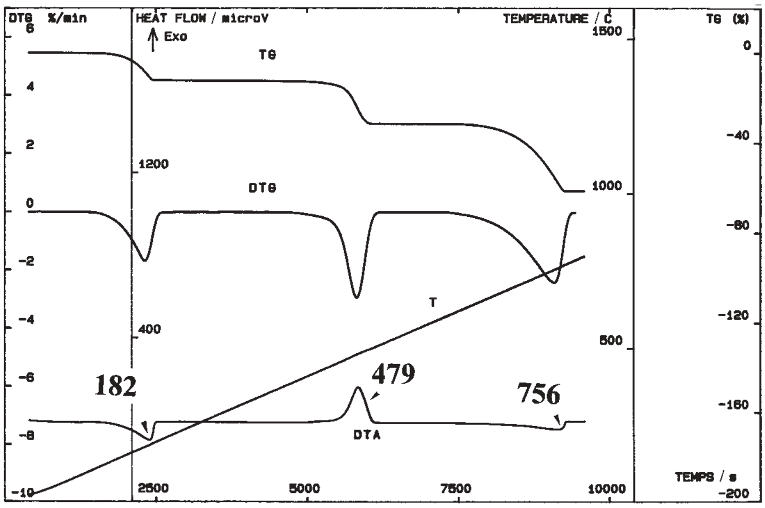

Fig. 1 TG, DTG, DTA curves of the calcium oxalate monohydrate – COM (air sweeping, sample 11.2 mg)

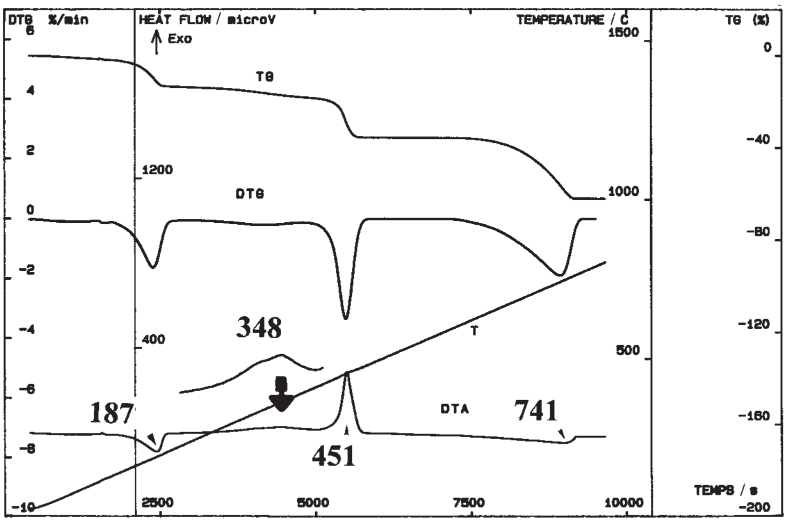

Fig. 2 TG, DTG, DTA curves of an urinary stone (COM) (air sweeping, sample 11.4 mg, the broad and small exothermic peak at 348°C is attributed to the non-crystalline organic compounds oxidation)

Calcium oxalate dihydrate (COD)

The thermal curves of a calcium oxalate dihydrate sample is in the Fig. 3 (under air sweeping). Two endothermic peaks, attributed to the water volatilization, are near 164 and 187°C. Then the same curves (DSC, TG) as for COM were observed.

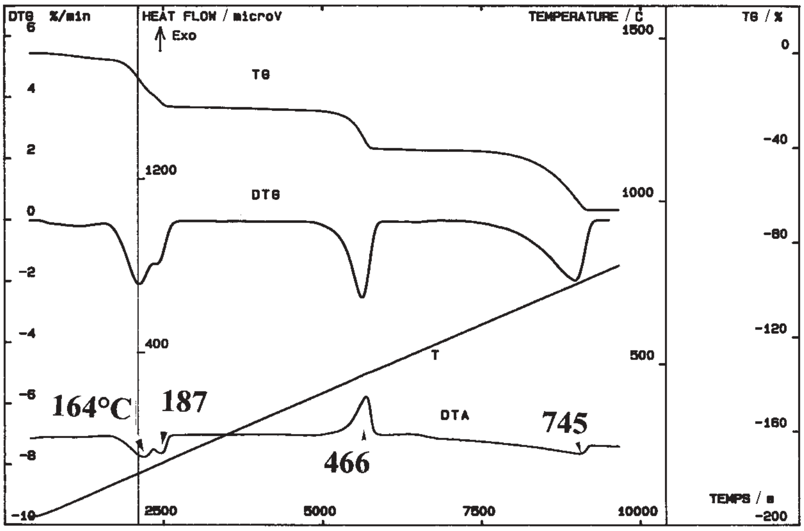

Fig. 3 TG, DTG, DTA curves of the calcium oxalate dihydrate (COD) (air sweeping, sample 12.2 mg)

Mixtures of COM and COD

Very often, the stones are mixtures of these two hydrates. It is difficult, to differentiate COM and COD in the binary mixtures, except when one of them is in little quantity in the calculi. A very low heating rate by DSC (0.3°C min^{-1}, from 100 to 180°C) permitted the differentiation of the two hydrate forms.

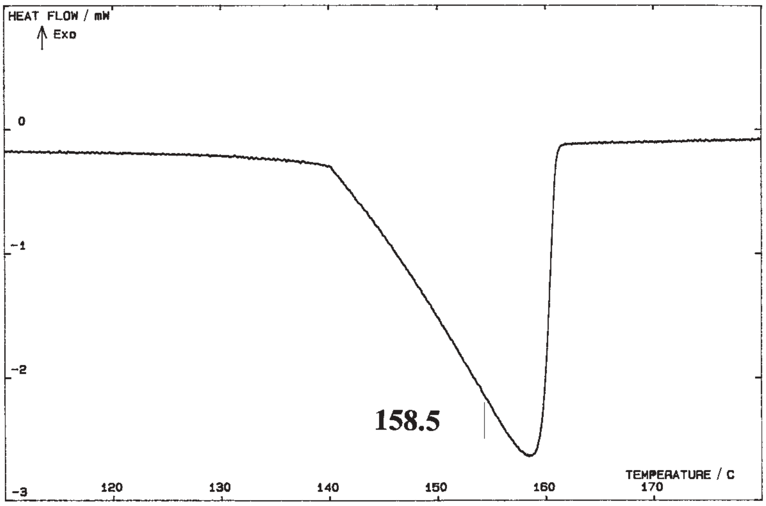

Fig. 4 DSC curve of the calcium oxalate monohydrate (COM) (sample 13.5 mg, 0.3°C min^{-1}, static air)

In Figs 4 and 5, the COM and the COD curves are presented: only one endothermic peak at 158.5°C for the COM and two endothermic peaks at 129.9 and 161.1°C.

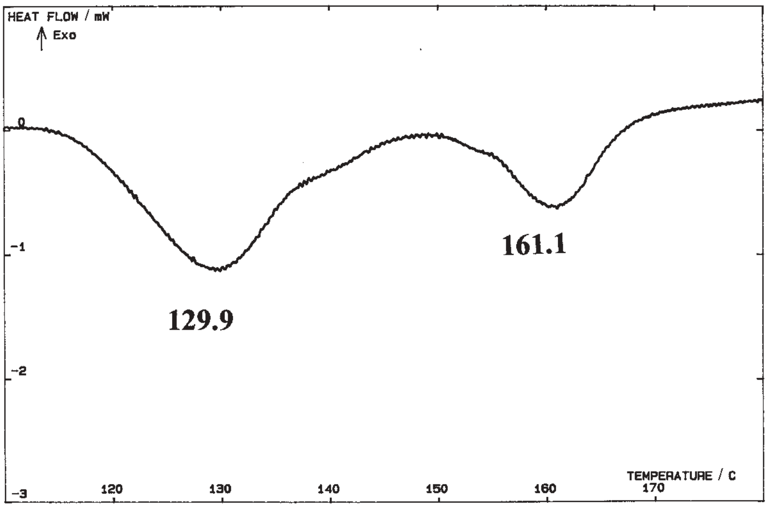

Fig. 5 DSC curve of the calcium oxalate dihydrate (COD) (purity 92%, sample 9.9 mg, 0.3°C min^{-1}, static air)

Twenty urinary calculi were analysed by DSC. In Fig. 6, three calculi DSC curves are shown. Three endothermic peaks are observed:

– the first one, between 128 and 131°C, can agree with the start of a water molecule from the COD;

– the second, between 155 and 162°C, can be attributed to the start of the water molecule from the COM;

– the third, between 159 and 166°C, can agree with the start of the second water molecule from the COD.

Several mixtures (50/50, mass/mass), obtained from urinary calculi, with pure COM and pure COD, showed the endothermic peak temperatures in these intervals presented before. This low heating rate (0.3°C min^{-1}) in DSC, can differentiate the two hydrates.

In Table 1, are the DTA mean results of 30 different urinary calculi. Tests were made under 0.5 L h^{-1} air sweeping, with about 10 mg samples and 5°C min^{-1} heating rate from ambient temperature to 850°C. The relative standard deviations are lower than 2%, for the exothermic peak and the last endothermic peak. On the other hand, the relative standard deviations are highest, in the cases of the first and the second endothermic peaks. More, if the available sample is lower than 2 mg, the peak temperatures are decreasing. In Table 1, are, also, presented the DSC mean results obtained on 20 different calculi. Tests were made under surrounding air, with about 10 mg samples, and 0.3°C min^{-1} as heating rate. The presence of the first endothermic peak

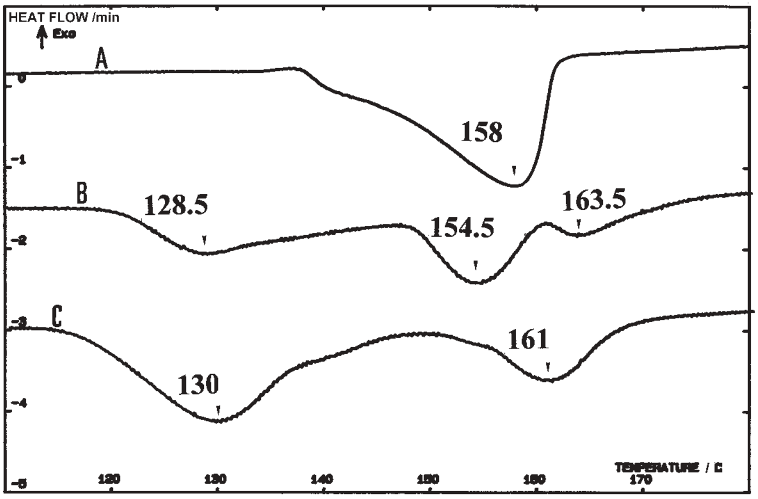

Fig. 6 DSC curves of urinary stones [*a*=11.7 mg (COM); *b*=10.3 mg (mixture of COM and COD); *c*=9.9 mg (COD); 0.3°C min^{-1}, static air]

is specific of the COD, in the stone. The second and the third endothermic peaks are near, respectively 158 and 163°C. The interest of the DSC technic is the good resolution of these two endothermic peaks: the first could be due to evolved water from the COM, and the second one, to the second evolved water molecule from the COD. So, the use of the calorimeter DSC, at very low heating rate, can differentiate these two very near peaks which are not separated by DTA, even with a very low heating rate.

Table 1 DTA and DSC results (maximum peak temperature) obtained on different urinary calculi. (By DTA (heating rate 5°C min^{-1}), are presented all the peaks observed from ambient temperature to 850°C. By DSC (heating rate 0.3°C min^{-1}), are presented all the peaks observed from 100 to 180°C)

DTA results (30 urinary calculi)	Endothermic peaks		Exothermic peak	Third endothermic peak
	first	second		
Average/°C	158	178	458	726
Standard deviation/°C	4.79	7.33	7.41	13.8
Relative standard deviation/%	3.03	4.12	1.62	1.90
DSC results (20 urinary calculi)	Endothermic peaks			
	first	second		third
Average/°C	130	158		163
Standard deviation/°C	2.03	2.29		2.20
Relative standard deviation/%	1.57	1.45		1.35

In decreasing the heating rate, the maximum first endothermic peak temperature was also decreasing: 130°C (by DSC, 0.3°C min^{-1}). In addition, the only second peak at 178°C, observed by DTA, can be divided into two peaks at lower temperature (158 and 163°C) by DSC.

Magnesium ammonium phosphate hexahydrate (MAPH)

The magnesium ammonium phosphate hexahydrate (MAPH) ($MgPO_4NH_4 \cdot 6H_2O$), showed the same thermal curves in air (Fig. 7) or in nitrogen sweeping, with an endothermic peak and an exothermic peak, by DTA. The first one is attributed to the loss of water and ammonia [19], the second one, to the magnesium pyrophosphate $Mg_2P_2O_7$ [20]. The transition from the 'amorphous' product to γ-crystalline form could explain this exothermic peak at 681°C [21]. The mass loss is 49.6% (theoretical 50.9%), from ambient temperature to 200°C, and 54.8% (theoretical 54.7%) from ambient temperature to 750°C.

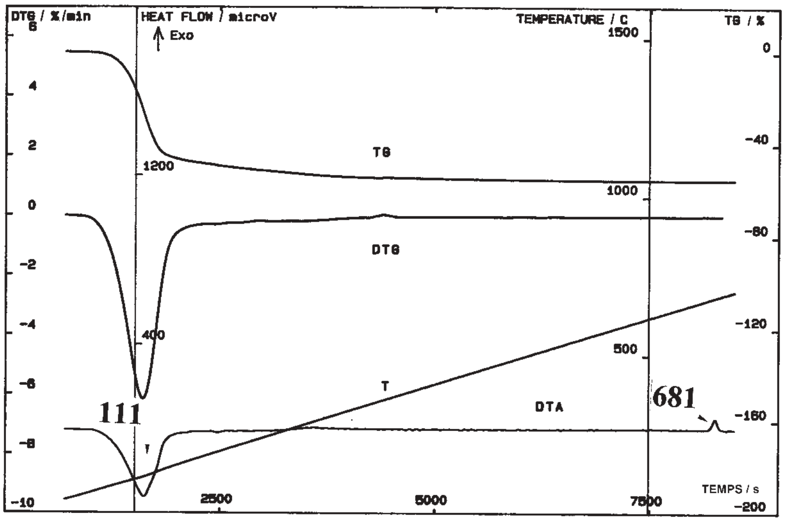

Fig. 7 TG, DTG, DTA curves of the magnesium ammonium phosphate hexahydrate (MAPH) (air sweeping, sample 11.9 mg)

The average of the peak temperatures, computed from five urinary stones of MAPH, were, respectively, 108 and 685°C. These values are very near those of the MAPH standard and those cited in [22].

The Fig. 8, under air sweeping, is corresponding to a renal calculus, with the presence of MAPH (endothermic peak at 116°C and exothermic peak at 686°C) and COM (endothermic peak at 186°C, exothermic peak at 473°C and broad endothermic peak at 735°C). A mixture (mass/mass) of 46% pure MAPH and 54% pure COM showed the same peaks. These two components can be differentiated. The small and broad exothermic peak at 314°C can be attributed to the organic compounds oxida-

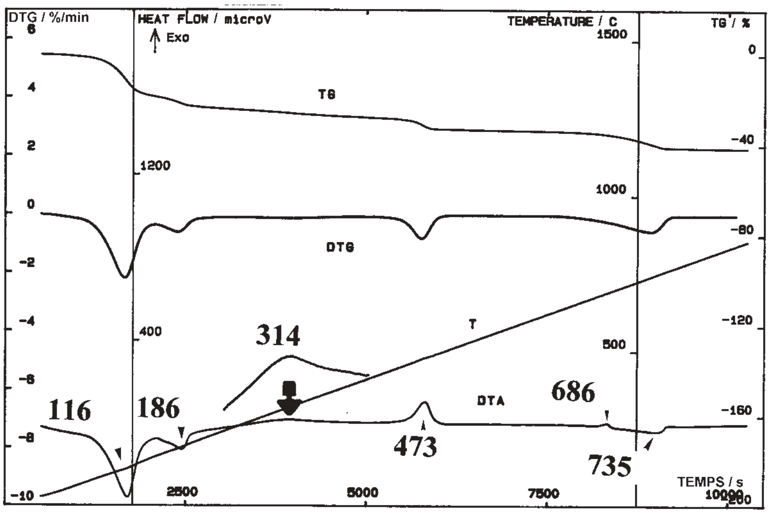

Fig. 8 TG, DTG, DTA curves of a urinary stone (mixture MAPH+COM) (air sweeping, sample 37.2 mg, the broad and small exothermic peak at 314°C is attributed to the non-crystalline organic compounds oxidation)

tion. Then, these identifications were confirmed by DSC: MAPH (endothermic peak at 88.5°C), COM (endothermic peak at 156.5°C) and urinary stone (endothermic peaks at 84 and 151°C).

Uric acid (UA)

We used only the anhydrous uric acid (UA) as standard. Pure UA showed an endothermic peak at 342°C and an exothermic peak at 451°C, by DTA, under air sweeping (Fig. 9). The TG, DTG and DTA curves were similar to those cited earlier [23]. Under nitrogen, the exothermic peak (corresponding to oxidation, or combustion, of the products evolved from the decomposition) was absent.

The urinary calculi showed, always, under air sweeping, these two specific DTA peaks. The average temperatures, computed from five urinary stones of UA, were, respectively, 418 and 446°C. The standards presented higher values: 429 and 450°C.

Quantitative analysis

TG-DTA analysis

The knowledge of the level of COM and COD, in the calcium oxalate stones, is very important for the clinician. So, it seemed that the expression of $Ca(COO)_2{\cdot}xH_2O$ is very judicious, x is corresponding to the number of molecule bounded water, with x comprised between 1 and 2. We neglected the case of the calcium oxalate trihydrate, because, it is very rare.

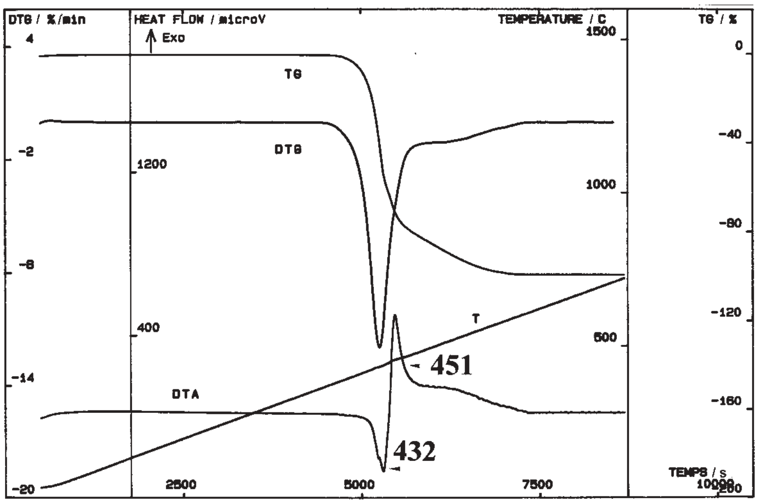

Fig. 9 TG, DTG, DTA curves of the uric acid (UA) (air sweeping, sample 10.8 mg)

In the study of the urinary stones, several intervals were considered, characterizing the mass losses. The boundary marks of these intervals agree with the temperatures of the DTG curve cancelling:

– from A (ambient temperature) to B (about 110°C) – free water (humidity);

– from B (110°C) to C (about 215°C) – bounded water (crystallized water) in COM and COD;

– from C (215°C) to D (about 400°C) – oxidation of organic compounds, always present, in few quantities;

– from D (400°C) to E (about 500°C) – decomposition of the calcium oxalate, with carbon monoxide evolution, which will be oxidized into carbon dioxide under air sweeping;

– from E (500°C) to F (about 800°C) – decomposition of the calcium carbonate, obtained in the last step, into calcium oxide and carbon dioxide.

Then, were determinated the number, respectively, of bounded water moles (step B to C), of carbon monoxide (step D to E) and of carbon dioxide (step E to F), for 100 g of urinary calculus. Finally, the following ratios were computed:

$$x_1 = \frac{\text{bounded H}_2\text{O (mol/100g)}}{\text{CO (mol/100g)}} \quad \text{and} \quad x_2 = \frac{\text{bounded H}_2\text{O (mol/100g)}}{\text{CO}_2\text{(mol/100g)}}$$

As an example, the results of the COM are presented. The averages of five assays are in the Table 2, with the consideration of molecular mass of H_2O (18.02), CO (28.01) and CO_2 (44.01).

Table 2 Quantitative TG results of the COM (averages from 5 tests, heating rate 5°C min^{-1}, under air sweeping)

Mass loss in the interval	B–C bounded H_2O/		D–E CO/		E–F CO_2/		Total mass loss/%
	%	mol/100 g	%	mol/100 g	%	mol/100 g	
Observed	12.2	0.677	19.0	0.678	29.8	0.677	61.0
Theoretical	12.33	0.684	19.17	0.684	30.12	0.684	61.6

From these experimental values, we deduced x_1=0.999 and x_2=1.000. The repeatability was done with 10 tests on the same urinary calculus (Table 3).

Table 3 Repeatability – DTA and TG results on the same urinary calculus (averages from 10 tests, heating rate 5°C min^{-1}, under air sweeping; *SD*=standard deviation, *RSD*=relative standard deviation in %)

DTA results (temperature)	Endothermic peak/°C bounded H_2O	Exothermic peak/°C organic compounds	Exothermic peak/°C, CO	Endothermic peak/°C, CO_2
Average	179	330	468	735
SD	1.78	0.92	1.14	4.11
RSD	0.99	0.28	0.24	0.56

TG results (mass loss)	B–C/		C–D/	D–E/		E–F	
	%	mol%	%	%	mol%	%	mol%
Average	12.63	0.701	5.28	13.87	0.495	19.74	0.448
SD	0.354	1.97	0.219	0.317	0.0113	0.414	0.0942
RSD	2.81	2.81	4.14	2.28	2.28	2.10	2.10

We computed x_1=1.415 and x_2=1.563. We deduced that the mass loss (expressed in mol%) is higher in the D–E interval, than the E–F interval. In fact, a part of the organic compounds was decomposed in the D–E interval, at the same time, the carbon monoxide was oxidized. So, we will choose, only the x_2 value, which agrees with the carbon dioxide evolution. In this case, x_2=1.563 corresponds to 56.3% of COD and 43.7% of COM, in the binary mixture of the two hydrated forms. The results, of another example, are in the Table 4.

From these results, we deduce x_1=1.055 and x_2=1.072. If we take into consideration, only, the x_2 value, we obtain 7.2% of COD and 92.8% of COM. The sum of all determinated products is:

$$3.08\%\ \text{(free water)}+11.48\%\ \text{(bounded water)}+$$
$$6.28\%\ \text{(organic compounds)}+0.594\cdot 128.1=96.9\%$$

where 128.1 is the molecular mass of anhydrous calcium oxalate.

Table 4 Quantitative TG results of an urinary calculus (heating rate 5°C min^{-1}, under air sweeping)

Intervals	Mass loss
A–B	3.08% of free water
B–C	11.48%=0.637 mol% of bounded water
C–D	6.28% of organic compounds
D–E	16.92%=0.604 mol% of carbon monoxide
E–F	26.13%=0.594 mol% of carbon dioxide

The remaining (3.1%) consists in calcium phosphate, determinated by chemical way; it cannot be characterized by thermal analysis because its high thermal stability.

The quantitative determination of calcium oxalate hydrate was earlier presented by Berényi and Liptay [18, 24]. If, in the expression $Ca(COO)_2 \cdot xH_2O$, x is near 1, the oxalate calcium stone is formed of COM in majority, in the case of 2, COD is in majority.

DSC technical

The DSC curve observed, in Fig. 5, was obtained on a sample (given by Daudon, Hôpital Necker, Paris – France) with 91.8 of COD and 8.2% of COM (so, x_2=1.918) and the sum of the determinated compounds was 98.9%. By linear integration of the areas under the DSC curves, the enthalpy's variations were:

ΔH_1=329.0 J g^{-1}, for the 1st endothermic peak (i.e. volatilization of one molecule of water in COD),

ΔH_2=132.1 J g^{-1}, for the 2nd endothermic peak (i.e. volatilization of the water in COM).

The ratio of the enthalpies $\Delta H_1/(\Delta H_1+\Delta H_2)$=0.714 was corresponding to the level of COD in the binary mixture COM+COD. From the TG values, the COD is at 91.8%. So, the corrected ratio of the enthalpies will be: k=0.714/0.918=0.778. We had obtained the repeatability of the DSC results of an urinary stone, in powdered form (Table 5) with a good relative standard deviation of 1.5%, for the ratio $\Delta H_1/\Sigma\Delta H$.

Table 5 Repeatability – DSC results on the same urinary calculus (10 tests, heating rate 0.3°C min^{-1}, under air surrounding; *SD*=standard deviation, *RSD* – relative standard deviation in %)

Temp. and ΔH	1st Endothermic peak		2nd Endothermic peak		3rd Endothermic peak		$\Delta H_1/\Sigma\Delta H$
	T/°C	ΔH_1/J g^{-1}	T/°C	ΔH_2/J g^{-1}	T/°C	ΔH_3/J g^{-1}	
Average	132	114.0	159	123.2	164	43.7	0.406
SD	0.95	3.49	1.61	3.50	1.71	1.48	0.00612
RSD	0.72	3.06	1.01	2.84	1.04	3.40	1.51

First, we observe, in Table 5, a good repeatability in temperature determination (about 1% as *RSD*). Then, the *RSD* of each enthalpy is about 3, and 1.51% for the ratio $\Delta H_1 / \Sigma\Delta H$. This last value is lower than that of mass loss: 2.10% as *RSD* in the E–F interval by TG (Table 3). The accuracy by DSC would be slightly better.

In this studied stone, the enthalpies ratio was 0.406, from which we deduced COD=(0.406/0.778)100=52.2% in the binary mixture, and *x*, determinated by DSC, will be 1.522 (instead of 1.563 by the TG method).

Two known mixtures, prepared from calculi and COM, had given *x* values very near:

– mixture 1*x*=1.457 (by TG) *x*=1.437 (by DSC);
– mixture 2*x*=1.278 (by TG) *x*=1.253 (by DSC).

The comparison of the two technics TG (gravimetry) and DSC (calorimetry) gives similar results of *x*. TG technic, with a higher heating rate (5°C min^{-1}), can characterize the different molecules in the stone. Even if the determination of water is easy by TG, the use of the calorimetry shows, clearly, a difference in the water volatilization temperature: about 159 for the COM and 164°C of the second molecule for the COD. The difference could explain a probable variation in the 'structure' of the 'original COM' and the 'COM issued from the COD'.

Correlation between TG and DSC technicals

Finally, from these mathematical models, we had computed, for 33 urinary calculi, the *x* values and the sum of the determinated compounds, by TG. The study showed:

– 20 calculi presented the sum of the determinated compounds between 90 and 101%, 6 between 70 and 89%, and 6 between 33 and 69%; 1 stone presented this sum upper 102% (the result was explained by a little sample of 2 mg);

– 18 calculi presented the x value located between 0.997 and 1.499, 14 between 1.500 and 2.027; 1 stone presented this *x* value at 2.124 (this result was explained by a low level of the calcium oxalate in the calculus).

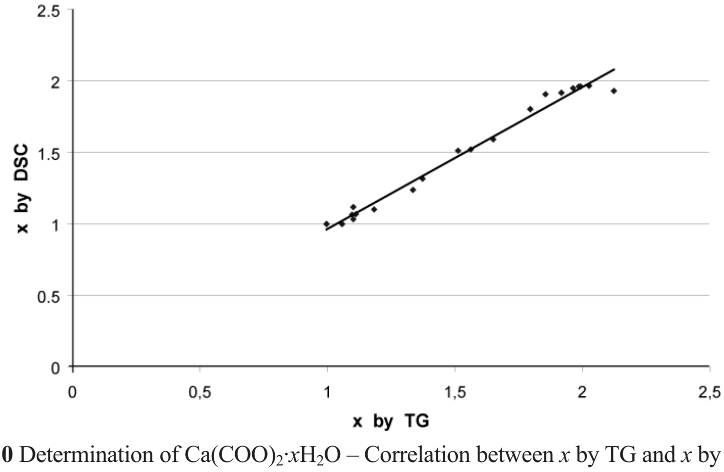

Fig. 10 Determination of $Ca(COO)_2{\cdot}xH_2O$ – Correlation between *x* by TG and *x* by DSC ($Y=0.9924\,X-0.0276$ with $Y=x$ (DSC) and $X=x$ (TG); $r=0.990$ with $p<0.001$)

For twenty calculi, were computed these x values, from the DSC curves. A very high significant correlation existed, for the x values, obtained, first, from the TG results, and secondly, from the DSC results (Fig. 10). The regression equation of the straight line was Y=0.9924X–0.0276 with Y=x(DSC) and X=x(TG); r=0.990 with p<0.001.

Conclusions

In our procedure, about 5 to 15 mg of each sample are necessary to realize a test by DTA-TG or by DSC. Each stone was ground and processed. Other tests by wet chemical and infrared analysis were performed, less sample could be used to characterize calcium oxalate hydrates and other compounds. But, the thermal analysis (DTA-TG or DSC) can lead to the knowledge of the quantity of each hydrate, in the mixtures, even if each one is not the major component. We showed that the quantitative analysis of urinary calculi, by DTA-TG method, is accurate. The DSC method could be used to confirm the data. The use of a calorimeter and a very low heating rate permitted the differentiation of evolved water at about 159 for the COM and at about 164°C from the COD. A very high significant correlation was observed in the results obtained between these two thermal analysis technicals. By the DTA-TG method, we can distinguish (with more than 90–95% accuracy), the amount of mono- *vs.* dihydrate, in calcium oxalate calculi. First, are compared the maximum peak temperature with those of standards and then the thermal analysis can successfully determine the relative percentage of COM and COD in pure calcium oxalate stone, but also, in some complex stone, containing calcium phosphate (without endothermic and exothermic peak by DTA, or mass loss by TG).

The knowledge of the true number of bounded water molecule to the calcium oxalate is very important to the clinician. A high level of calcium COD (or Weddelite) in the urinary stones leads inflammation, sharp pain and blood in urine. In the worse cases, they must be extracted by surgical way.

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