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THERMOGRAVIMETRIC ANALYSIS OF HUMAN RENAL CALCULI SAMPLED IN NINETEENTH CENTURY PATIENTS
Discussion on the basis of their alimentary customs

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TG and DTG curves of human renal calculi of patients living in the nineteenth century in the South of Italy are reported and compared with those of presentday patients. Marked differences in calculi composition are found in the two different historical periods, that are hypothetically discussed in terms of different diets and of alimentary customs of countries of the considered patients.

Keywords: human renal calculi

Introduction

Human renal calculi in patients living last century in the South of Italy and drawn between 1891 and 1894 where quantitatively analysed by thermogravimetric analysis (TG and DTG). Thermal analysis of renal calculi was first suggested several years ago by Strates [1]. Later, the Hungarian school of thermal analysis performed interesting research involving the analysis of renal calculi using thermal methods [2]. Lastly, some authors of this paper and other researchers of the Chemistry Department of Rome University 'La Sapienza' used thermoanalytical techniques [3] to analyse synthetic mixtures of the main constituents of renal calculi, designed to simulate real calculi. They examined the reliability and confidence of the TG method for the quantitative analysis of the renal calculi. In the present work we carried out TG and DTG analysis of thirteen calculi belonging to 19th century patients in order to ascertain whether there is any statistical difference between the main constituents of the calculi sampled in

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the 19th century patients in the South of Italy and those from patients living in several different countries in the present age.

Experimental

TG and DTG curves of the renal calculi were obtained using a Mettler TG 50 thermobalance coupled with a Mettler TG 10A-TA processor system and a Swiss dot-matrix printer (Figs 1–3), or with a DuPont model 951 thermobalance (Figs 4 and 5) and, with a Mettler DSC 20, the DSC curve shown in Fig. 2. TG measurements were carried out in the range between room temperature and 900°C in an air stream (flow rate 100 $cm^3 \cdot min^{-1}$) at a heating rate of 10 $deg \cdot min^{-1}$.

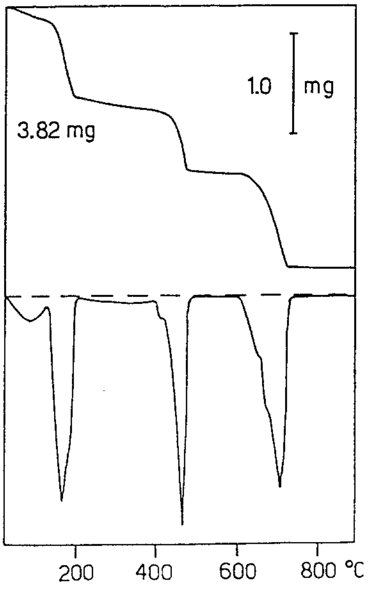

Fig. 1 TG and DTG curves for the analysis of a typical renal calculus belonging to a contemporary patient and practically constituted only of hydrated calcium oxalate. Air flow 100 $cm^3 \cdot min^{-1}$, heating rate 10 $deg \cdot min^{-1}$

Qualitative chemical colorimetric tests to recover cationic, anionic and organic species were performed with a Merckognost *n.* 11003 commercial kit, supplied by Merck (Darmstadt). The samples analysed comprised thirteen human renal calculi, stored in greaseproof paper envelopes. The calculi had been removed from patients having lived at the end of the nineteenth century in the South of Italy, especially in Sicily. Two further calculi, indicated as typical examples of 'modern calculi' were obtained from the Urological Clinic of the

University of Rome 'La Sapienza'. Samples were carefully broken up into coarse pieces, homogenized and directly analysed by TG technique in platinum or aluminium oxide crucibles.

Method

Qualitative and quantitative data concerning the main constituents of the calculi were obtained using the same procedure. Analysis of the TG curves of renal calculi was performed using the same criteria as those discussed in a previous paper [3] in which thermal analysis of synthetic mixtures and natural human calculi were studied in detail. In several cases human renal calculi are composed of only one component, making TG analysis very easy, as the TG curve of the sample is compared with that of the pure component. For example, if the TG and DTG curves of natural calculi display three typical steps, located in the temperature ranges of about 150°–200°, 395°–500° and 670°–765°C respectively [3], this identifies calcium oxalate hydrate as the component of this type of renal calculus.

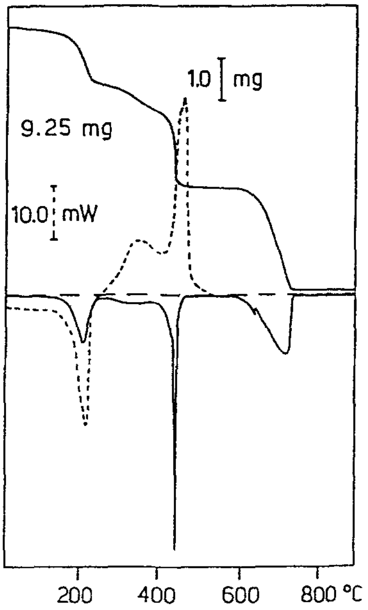

Fig. 2 TG and DTG curves for the analysis of a typical renal calculus belonging to a contemporary patient and practically constituted of hydrated calcium oxalate and containing about 6% w/w of organic substance. Air flow 100 $cm^3 \cdot min^{-1}$, heating rate 10 $deg \cdot min^{-1}$; dot curve = DSC curve, from 25° and 600°C in an air flow of 100 $cm^3 \cdot min^{-1}$, heating rate 10 $deg \cdot min^{-1}$; sample weight = 10.5 mg

Conversely, if the TG curve display only one large step in the range of 380°–590°C and DTG curve peaks at about 430°–440°C, this identifies the TG curve as that corresponding to uric acid [3]. All the thermal data of the other main constituents of renal calculi were also accurately described using the same procedure in the previous paper [3]. Moreover, since the thermal decomposition process involving different substances present in the renal calculi may fall within the same temperature range, so that the TG steps overlap, it may be necessary to set and to solve a system of equations. Two or three are actually enough for calculi as generally not more than three components are present in addition to included organic substances [3].

Results

TG and DTG curves of two present-day typical renal calculi are reported in Figs. 1 and 2, while Fig. 3 shows the characteristic TG and DTG curves of two typical renal calculi of 19th century patients living in the South of Italy. It can be observed that both TG curves of the Fig. 3 show only one large step at about 430°C, while both the curves shown in Figs 1 and 2 display three steps, at 130°–220°, 400°–470° and 600°–740°C, respectively. It may thus be inferred that the two calculi of contemporary patients (particularly the first) consist mainly of pure hydrated calcium oxalate, or (the second one) of oxalate and of organic sub-

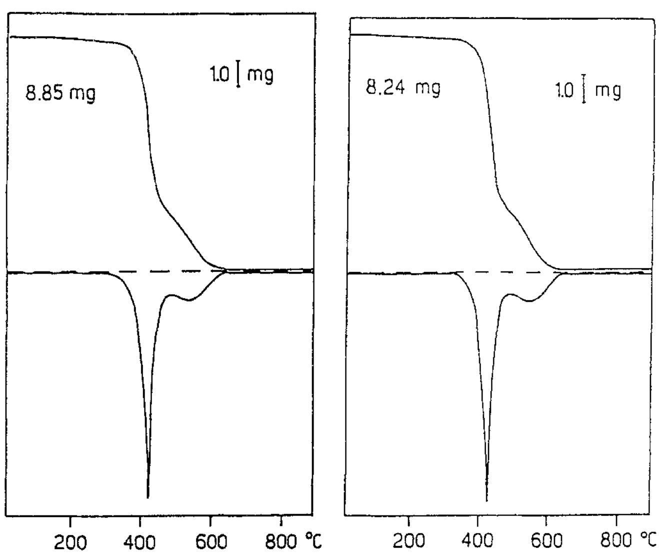

Fig. 3 TG and DTG curves for the analysis of two typical renal calculi belonging to a patient from last century mainly constituted of urates. Air flow 100 $cm^3 \cdot min^{-1}$, heating rate 10 $deg \cdot min^{-1}$

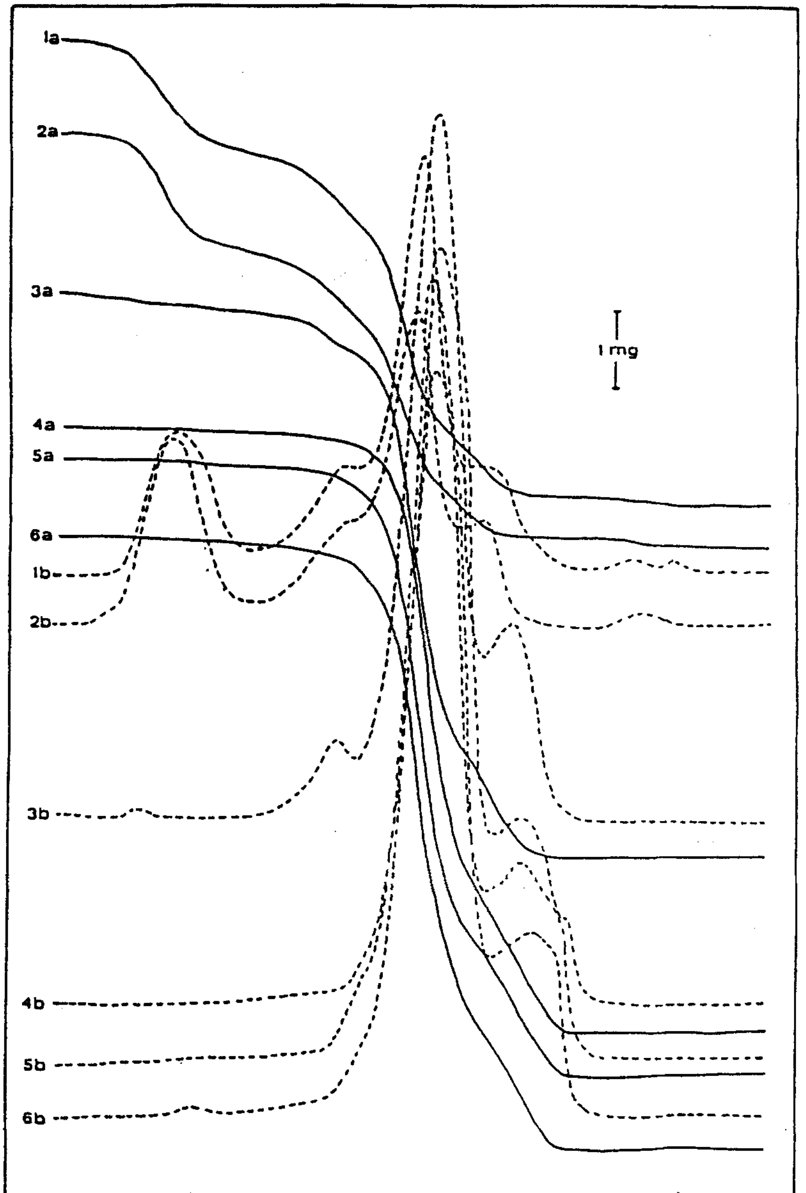

Fig. 4 TG (*a*) curves and DTG (*b*) curves for the analysis of sic renal calculi from last century. Air flow 100 $cm^3 \cdot min^{-1}$, heating rate 10 $deg \cdot min^{-1}$
Sample 1 = 8.1 mg; 2 = 7.8 mg; 3 = 7.8 mg; 4 = 7.9 mg; 5 = 8.0 mg; 6 = 8.1 mg

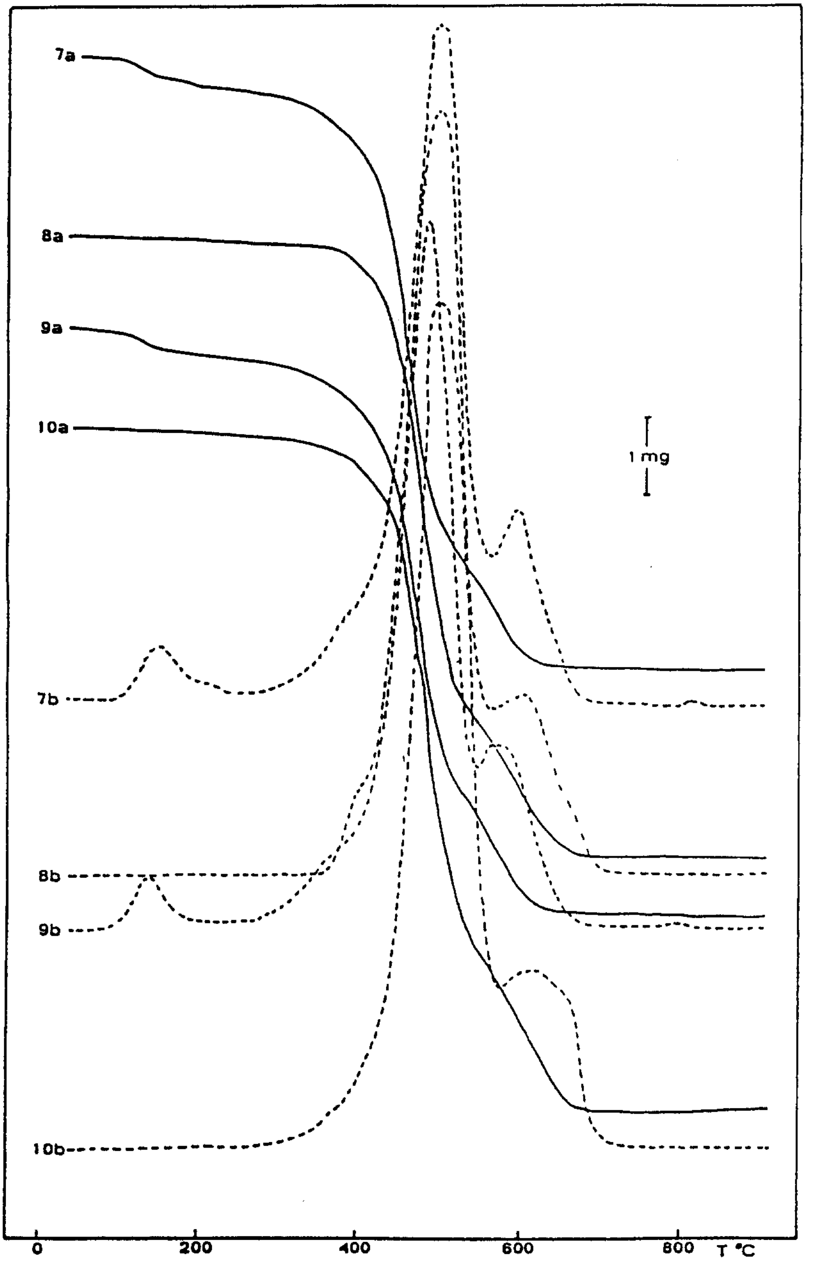

Fig. 5 TG (*a*) curves and DTG (*b*) curves for the analysis of four renal calculi from last century. Air flow 100 $cm^3 \cdot min^{-1}$, heating rate 10 $deg \cdot min^{-1}$.
Sample 7 = 8.6 mg; 8 = 8.0 mg; 9 = 8.4 mg; 10 = 9.0 mg

Table 1 Renal calculi of the last century. Qualitative analysis by colorimetric tests

Sample	Year	CO_3^{2-}	Cystine	PO_4^{3-}	Mg^{2+}	Ca^{2+}	NH_4^+	Uric acid	Oxalate
1	1894	–	–	+	+	+	+	+	+
2	1894	–	–	+	–	+	+	+	–
3	1894	–	–	–	–	–	–	+	–
4	1894	–	–	–	–	–	–	+	–
5	1893	–	–	–	–	–	–	+	–
6	1891	–	–	+	–	+	+	+	+
7	1893	–	–	+	–	+	+	+	+
8	1893	–	–	–	–	–	+	+	–
9	1894	–	–	–	–	+	+	+	+
10	1894	–	–	+	–	+	+	+	–
11	1894	–	–	–	–	–	+	+	–
12	1893	–	–	–	–	–	+	+	–
13	1894	–	–	+	+	+	+	+	+

(+) found

(–) not foun d

Table 2 Results, by TG analysis, of the composition of thirteen renal calculi of the last century

Sample *n*	Year	Calcium oxalate %	Calcium phosphate %	Ammonium magnesium phosphate %	Uric acid % (A)	Ammonium urate % (B)	Sodium urate % (C)	Organic substances % (D)	Tot. % (A →D)
1	1894	4		48	A	+ B	+ C		48
2	1894		12		A(33)	+ B(55)			88
3	1894				A				100
4	1894				A				100
5	1893				A				100
6	1891				A				100
7	1893	1	19		A	+ B	+ D		80
8	1893				A	+ B	+ D		100
9	1894	1	13		A	+ B	+ D		86
10	1894		2		A	+ B	+ D		98
11	1894				A(90)	+ B(10)			100
12	1893				A(72)	+ B(28)			100
13	1894	4	11	36	A	+ B			49

Numbers in brackets indicate found percent value of constituents ((A) or (B), respectively) while number s in the column (A →D) indicate the sum of the found percent values of the constituents, from (A) to (D), which are present in the examined sample.

Table 3 Percent number of presences of each main constituent of renal calculi, with reference to our data, found by examining the thirteen samples of the last century and to bibliographic Ref. [5], for present-day calculi

Calculi composition	(Age of samples: ≈ 1980) % number of presences reported in literature [5]	(Age of samples: ≈ 1890) % number of presences found by us
Calcium oxalate	24	0
Calcium oxalate + calcium phosphate	43.5	0
Calcium oxalate + urate	8	0
Cystine	0.5	0
Calcium phosphate	5	0
Ammonium magnesium phosphate	8	0
Calcium oxalate + ammonium magnesium phosphate + urate	0	8
Urate + calcium phosphate	0	23
Uric acid + urate	9	46
Urate + calcium oxalate + calcium phosphate	0	15
Others	2	8

stances (6% by weight). The latter is evidenced by a step at 260°–385°C in the TG and DTG curves and by the small exothermic peak between the same temperatures in the DSC curve in Fig. 2, while other two greater peaks, in the DSC curve, are well known as typical respectively for the water loss and for the decomposition, on air, of the oxalate into carbonate [4]. On the basis of the previous discussion and of the TG curve of the pure substance reported in the previous paper [3], the thermogravimetric curves shown in Fig. 3 clearly show, on the contrary, that the two calculi of the 19th century patients are constituted mainly of uric acid, according with results well known in literature [5]. The TG and DTG curves of ten of the thirteen examined calculi, from the last century patients living in the South of Italy, are reported in Figs 4 and 5. The thermogravimetric results, confirmed and supported by the chemical colorimetric qualitative tests, reported in Table 1 for NH_4^+, Mg^{2+}, Ca^{2+}, PO_4^{3-}, CO_3^{2-}, oxalate, uric acid and cystine, are summarized in Table 2. Lastly, in Table 3, for each main component of the calculi, the percent number of presences are shown with reference both to our data, obtained by examining the thirteen samples of nineteenth century patients, and to bibliographic references for a great number of 'modern calculi' [5].

Discussion

Results confirmed the validity of the TG techniques in this field of application and of the criteria adopted for TG curve evaluation. The data reported in Table 3 confirm, also statistically, what has already seen when comparing curves of contemporary patients' calculi, for instance those ones show in Figs 1 and 2, with those of last-century patients (Fig. 3). In fact, the compositions of the renal calculi found for patients having lived in the South of Italy during the last century, when compared with those belonging to patients living in our century and in several countries, reveal a more marked presence of uric acid and urates in the former and of oxalate in the latter. There are well grounded suspicions that these differences can be hypothetically ascribed to the patients' different diets and countries. In particular, the diets of the patients of the last century living in the South of Italy seem to be more suitable for producing urate calculi, while contemporary diets are more likely to produce oxalate calculi, irrespective of the country. The presence of oxalate, mainly as calcium oxalate, in modern calculi can be easily explained by a diet based on certain vegetables (i.e. tomatoes, spinachs, celeries, carrots and beetroots), fruits (oranges, straw-berries and raspberries), potions (tea, coffee) and chocolate [6]. On the other hand, it is not so easy to correlate food intake with the composition of the calculi of last century patients. In fact, the occurrence of urates in biological fluids is known to be generally related to a diet essentially based on meat. Nevertheless, such a diet was unlikely to be followed by people living in the last century, especially in underdeveloped areas such as southern Italy. On the other hand, urates are extensively present in some fish species (anchovies, sardines, herrings) and animal entrails [7], which were certainly present in the diet of people living in the South of Italy and in particular in Sicily. Also urates coming from legumes (lentils and kidney-beans) [7] have to be taken into account. Lastly, the influence of genetic factors cannot be excluded, in view of the very limited zones of origin of the calculi samples from last century.

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Zusammenfassung — TG- und DTG-Kurven von menschlichen Nierensteinen von Patienten aus dem neunzehnten Jahrhundert aus Süditalien wurden beschrieben und mit denen von heutigen Patienten verglichen. Für diese zwei verschiedenen Geschichtsabschnitte wurden wesentliche Unterschiede der Steinzusammensetzung gefunden, was hypothetisch als Folge unterschiedlicher Ernährung und Ernährungsgewohnheiten der Länder dieser Patienten interpretiert wird.