# Thermochromatography for evolved gas analysis of apatite materials

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## Abstract

Evolved gas analyses of model inorganic compounds and apatites are described. The measurements were performed on a system comprising a 'thermochromatograph', with a low-volume thermal furnace, interfaced to a capillary gas chromatograph via a computer-controlled, pneumatic sample inlet device in the temperature region 70–600°C. The performance of this inherently simpler system is comparable to that of thermogravimetry but is superior in resolving possible reactions when similar materials are analysed.  © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

An ideal evolved gas analysis (EGA) instrument would provide a time- or temperature-based record of the appearance and disappearance of all evolved compounds, together with their identification. Although the instruments combining thermogravimetry and mass- or infrared spectrometry [1,2] can continuously monitor the evolved products with scan speeds of fractions of a second, their complete capability may only be required when the evolved gas composition is a truly complex mixture. Even then, better resolution, in terms of non-collinear information content revealed, might be achieved by a thermogravimetry–gas chromatography–spectrometry (TG–GC–MS/IR) system [3]. On the other hand, many EGA applications, especially those for inorganic samples, have relatively simple and predictable evolved gas compositions and the justification for spectrometric identification tools is not clear. In addition to the high cost per sample, these seemingly

more sophisticated approaches add several problems: (a) the relatively large TG furnace volume can degrade system performance for narrow EGA peak shapes, (b) potential sample component loss in long interconnecting lines between TG and IR or MS instruments because of condensation.

Koel et al. [4] have demonstrated that many of the common goals of EGA can be met by total computer control of the experiment using a small-volume reactor and a gas chromatograph as the detection method. Their method, by analogy to other hyphenated analytical techniques, is called thermochromatography (ThGC) and corresponding surface plots are thermo(gas)-chromatograms. Cited previous work demonstrated good performance of ThGC in cases where the sudden evolution of gas-phase materials occurs. A clear advantage of possible gas chromatographic separation is seen in cases studying the degradation products of calcium oxalate, where a secondary reaction of disproportionation of CO to $CO_2$ and C take place and the products are seen on chromatograms. Despite its many attractive features, using GC as an EGA detector introduces at least two more problems. First is the detection of the evolved

compounds in the case of samples that release only small amounts of gas during their heating (relative to their total mass), as is the case for many inorganic samples. Second is that separation of the evolved components requires careful selection of the GC column, to avoid selective trapping in the column.

## 2. Experimental

A schematic diagram of the overall system is presented in Fig. 1. The quartz tube furnace, which replaces the injection port of the chromatograph, has a volume of 4 ml and the sample is located here. The
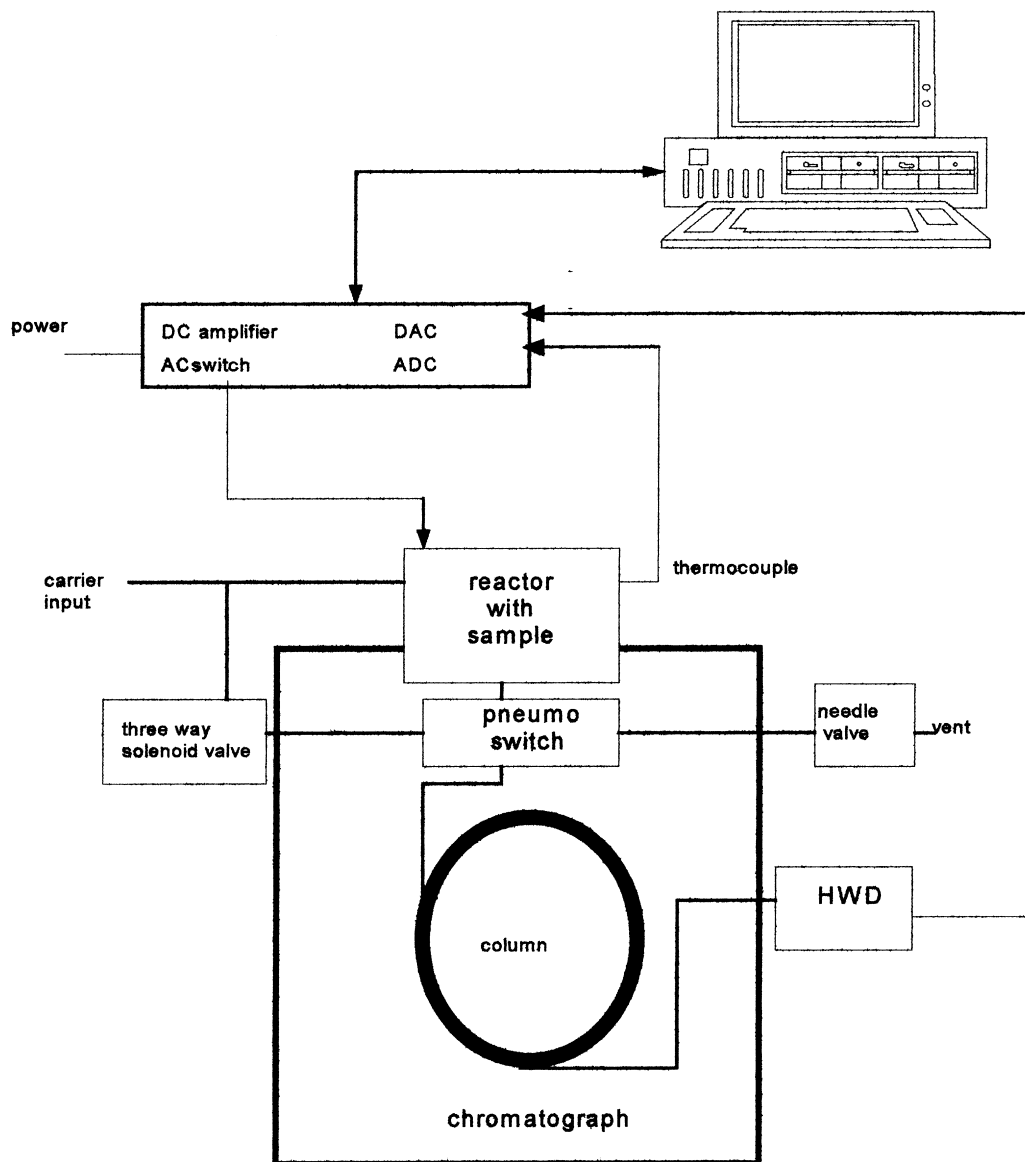


Fig. 1. Schematic diagram of the thermochromatographic experiment.

furnace/reactor temperature is controlled by a separate, stand-alone temperature programmer with an operating range of 70–600°C, at heating rates of 1–25°C/min. In our experiments, a heating rate of 10°C/min was used in the temperature region from 70 to 600°C for all samples. Commercial programmed temperature vaporisation injectors (PTV), which can be used both as a thermo-desorption unit and as a programmed pyrolyser [5] at temperatures up to 600°C, are now available.

Automatic injection of the evolved gas onto the GC column must be achieved at relatively high temperatures, to match common GC column inlet operating conditions. Because of the constant problem of wear-and-tear in this experimental scheme, an alternative to mechanical valves and sampling was used, i.e. a pneumatic sampling valve with no moving parts, however, this was at the expense of some further sample dilution. Such samplers operate on the principle of carefully balancing the pressures in the sample stream and the carrier gas flow and were first described by Deans [6] and are used in this system to introduce the aliquots of sample head space into the capillary column. A complete description of the sampler is given in earlier work [7]. The chromatograph is a Carlo Erba 4200 GC system with a thermal conductivity detector (model 430), which has fast electronics. The choice of column for chromatographic separation was based on the need for fast, high efficiency resolution of components with different polarities, such as carbon dioxide, water and ammonia. From previous experience in the separation of gases, Porapack Q-packed columns were known to exhibit good behaviour. In the case of ThGC, the sample size is limited and capillary columns are better suited for these tasks. All this led us to look for suitable capillary columns. The wide-bore PLOT column with a porous polymer layer has these types of properties [8]. A porous layer column, 25 m×0.53 mm I.D. (NSW-PLOT; HNU Nordion, Finland) was used to separate gaseous products of decomposition. The separation of carbon monoxide and carbon dioxide, as well as the separation of water and ammonia, was achieved in the same run at a relatively high temperature (70°C). The separation of the evolved products of degradation of ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$) are given as an example
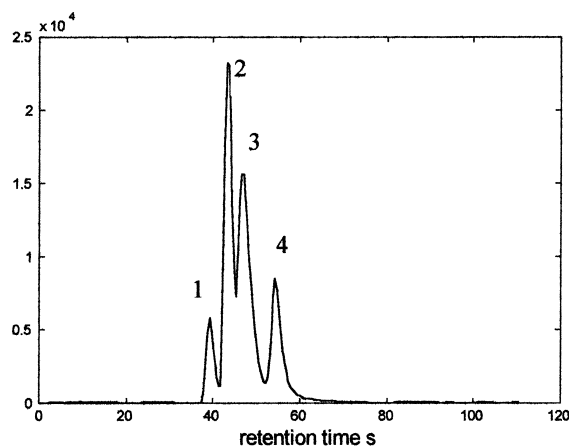


Fig. 2. Chromatogram of the thermal decomposition products of ammonium oxalate at a temperature of 205°C. (1) CO; (2) $CO_2$; (3) $NH_3$; (4) $H_2O$.

(Fig. 2). The column used gave some tailing for water and ammonia, and showed some irreversible adsorption of ammonia over time, however, with proper calibration, it was possible to get good quantitative results and this was the main reason that a systematic study on other columns was not conducted. The column temperature was isothermal at 70°C during the experiment. The sampling valve was in the column oven and was at the same temperature as the column.

Sampling is controlled by a computer and by an interface card that was manufactured locally. The sampling events occur at intervals equal to the separation time of the evolved components (total chromatogram runtime was 110 s in our case) and then chromatograms of the evolved gases are associated with certain temperatures. The detector signal is converted to digital form and transferred to a 486-type personal computer over an RS232 interface for final data processing. At first, the image processing methods display such EGA response surfaces as two-dimensional (2D) objects, either as contour or mesh plots. In Fig. 3 the thermochromatogram of magnesium ammonium carbonate apatite (sample 3) is presented as a mesh plot. Although such plots do not add much to the final presentation of the EGA results (the evolution rates of the released gas
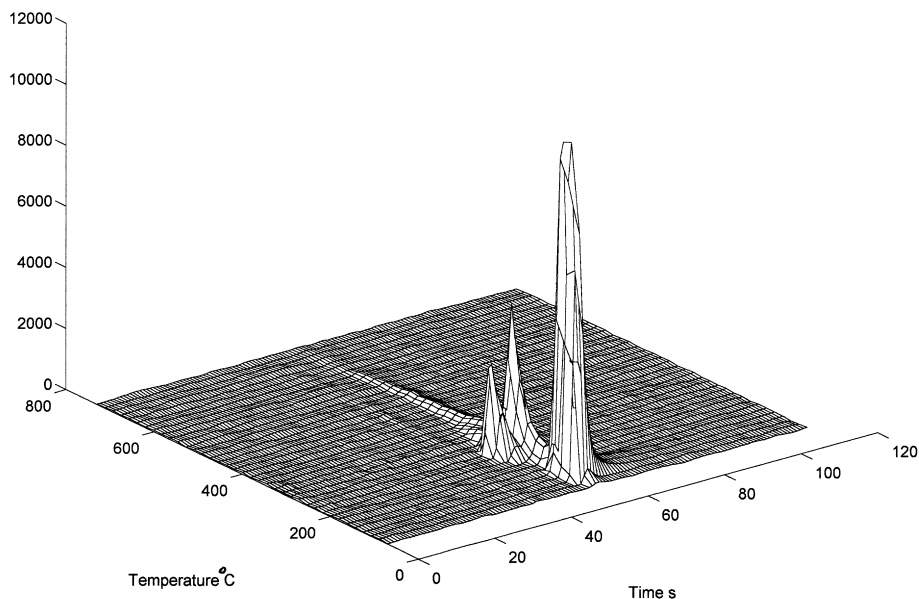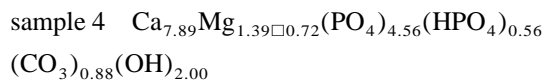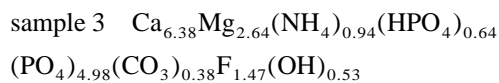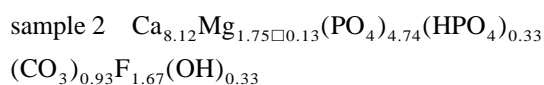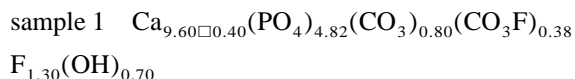
Fig. 3. Mesh plot of magnesium ammonium carbonate apatite degradation products: the peak at a retention time of 45 s corresponds to $CO_2$, that at 55 s corresponds to $NH_3$, and that at 60 s corresponds to $H_2O$.

components as a function of sample temperature) they do provide a convenient 'picture' for the analyst of the thermal events occurring in the sample.

The authors wrote most of the software used (available upon request). Equipment control (sampling and data recording) software was written in assembly language. When necessary, chromatogram preprocessing (baseline correction, spike removal, digital filtering, etc.) was performed using software that was written in C. MATLAB (MathWorks, Natick, MA, USA) was used for the 2D representation of thermochromatograms.

Two inorganic reagents, $MgNH_4PO_4 \cdot 6H_2O$ (Fluka, Buchs, Switzerland) and $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ (Reachim, Moscow, Russia), and four samples of synthetic carbonate apatites, synthesised in Tallinn Technical University, were studied. The apatite samples were synthesised using the precipitation method described previously [9,10]. The apatites were identified by X-ray diffraction (XRD) and IR spectroscopy as B-type carbonate apatites ($CO_3^{2-}$ substituted for $PO_4^{3-}$). The formulae of the samples, calculated using chemical analysis data and according to the electroneutrality principle, are as follows:

sample 1 $\quad Ca_{9.60\square 0.40}(PO_4)_{4.82}(CO_3)_{0.80}(CO_3F)_{0.38}$ $F_{1.30}(OH)_{0.70}$

sample 2 $\quad Ca_{8.12}Mg_{1.75\square 0.13}(PO_4)_{4.74}(HPO_4)_{0.33}$ $(CO_3)_{0.93}F_{1.67}(OH)_{0.33}$

sample 3 $\quad Ca_{6.38}Mg_{2.64}(NH_4)_{0.94}(HPO_4)_{0.64}$ $(PO_4)_{4.98}(CO_3)_{0.38}F_{1.47}(OH)_{0.53}$

sample 4 $\quad Ca_{7.89}Mg_{1.39\square 0.72}(PO_4)_{4.56}(HPO_4)_{0.56}$ $(CO_3)_{0.88}(OH)_{2.00}$

The samples were placed in a quartz vial inside the reactor and the weight of the sample was about 20 mg.

## 3. Results and discussion

### 3.1. Decomposition of salts

The goal of the work was to show the ability of ThGC to provide a lot of information for the better understanding of the thermal decomposition of apa-

tites. The hope was that the known thermal chemistry of some salts would aid in the interpretation.

By the thermal analysis of ammonium salts, ammonia is evolved, along with water, as part of the total weight loss at the same temperature. If each evolution process is to be distinguished, there are distinct advantages in obtaining separate evolution curves. In this case, ThGC offers a simpler solution to the detection of simultaneous evolving gases than, for example, the approach of Paulik et al. [11], who used thermo-gas titrimetry (TGT).

Considering this type of apatite, magnesium am-

monium phosphate hexahydrate was chosen as a model because of its relatively complex process of degradation. On the evolving curve of ThGC (Fig. 4), one can follow three peaks: (1) in the temperature region 90–190°C, when water is evolving (73.7% of the total amount); (2) in the temperature region 240–320°C, when water (23.1% of the total amount) and ammonia are evolving simultaneously; (3) in the wide temperature region 450–570°C, when water is evolving (3.2%). These data indicate that the release of five water molecules and the decomposition of the intermediate, $MgNH_4PO_4 \cdot H_2O$, were
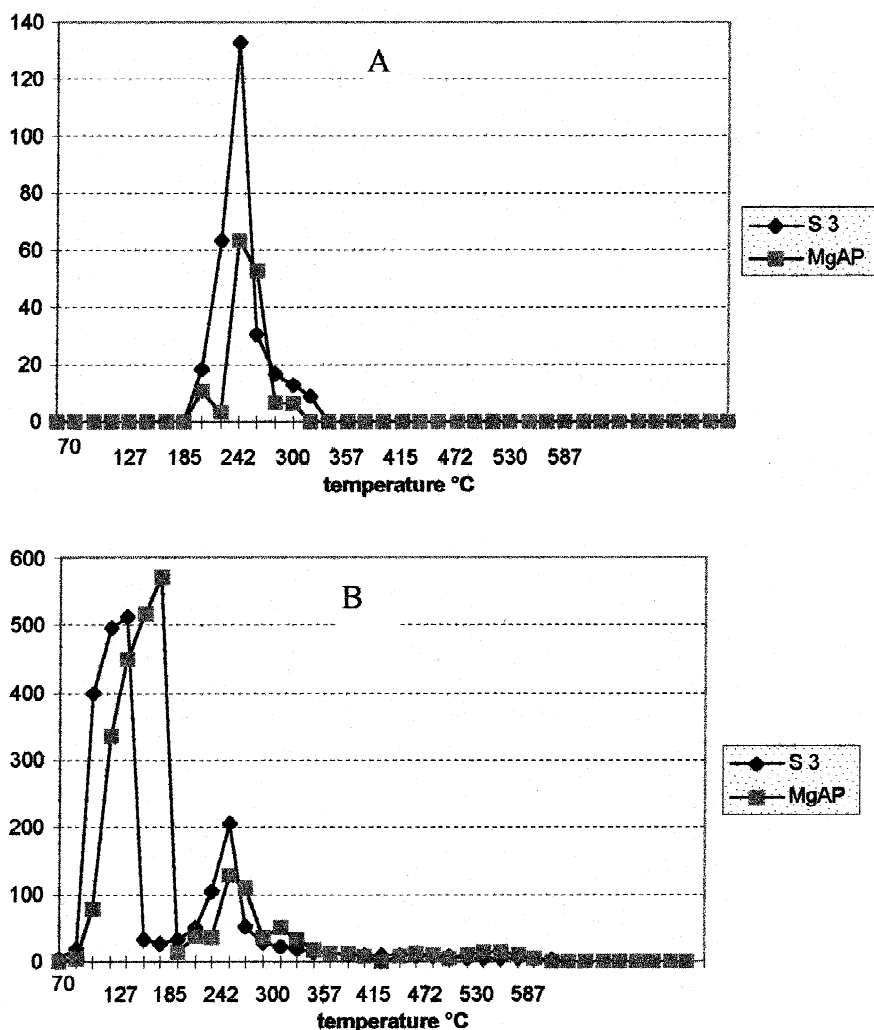


Fig. 4. Thermal decomposition of magnesium ammonium phosphate (MgAP) and carbonate apatite sample 3 (S3): (A) evolution of $NH_3$; (B) evolution of $H_2O$.

well separated and that a part of the water of hydration remained and evolved simultaneously with ammonia. This evolution took place in the temperature region 240–320°C. Using peak height, the amount of water evolving in that region was determined to be approximately $1\frac{1}{2}$ molecules and corresponds to the main reactions:

$$MgNH_4PO_4 \cdot H_2O \Rightarrow MgNH_4PO_4 + H_2O$$

$$2MgNH_4PO_4 \Rightarrow Mg_2P_2O_7 + 2NH_3 + H_2O$$
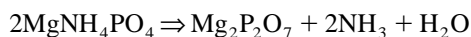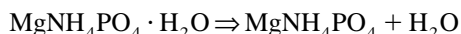
The existence of the third step at higher temperatures (450–570°C) shows the evolution of some part of the remaining constitutional water. It means that hydrous intermediate(s) are formed during the second step:

$$MgNH_4PO_4 \Rightarrow MgHPO_4 + NH_3 \text{ or}$$

$$4MgNH_4PO_4 \Rightarrow MgH_2P_2O_7 + Mg_3(PO_4)_2 + 4NH_3 + H_2O,$$
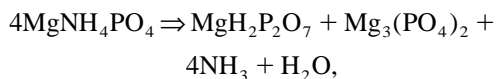
and that these partial processes were not separated.

These intermediates decompose at higher temperatures and lead to the evolution of water in the third step:

$$2MgHPO_4 \Rightarrow Mg_2P_2O_7 + H_2O \text{ or}$$

$$2MgH_2P_2O_7 \Rightarrow Mg_2P_4O_{12} + 2H_2O$$
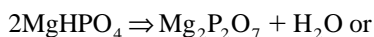
From the evolved gas analysis alone, it is sometimes hard to identify the reactions and one must use other analytical methods, such as IR or X-ray spectroscopy for solids to confirm the final products.

Magnesium carbonate hydroxide hydrate $[4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O]$ belongs to a group of aquoxides with a complicated crystal structure and they commonly exhibit multistage decomposition [12]. The total evolution curve (Fig. 5) for the ThGC of magnesium carbonate hydroxide hydrate has three distinct steps, all of which proceed consecutively, with some overlap: (1) mainly water and some $CO_2$ are evolving in the range 220–335°C; (2) $CO_2$ and a
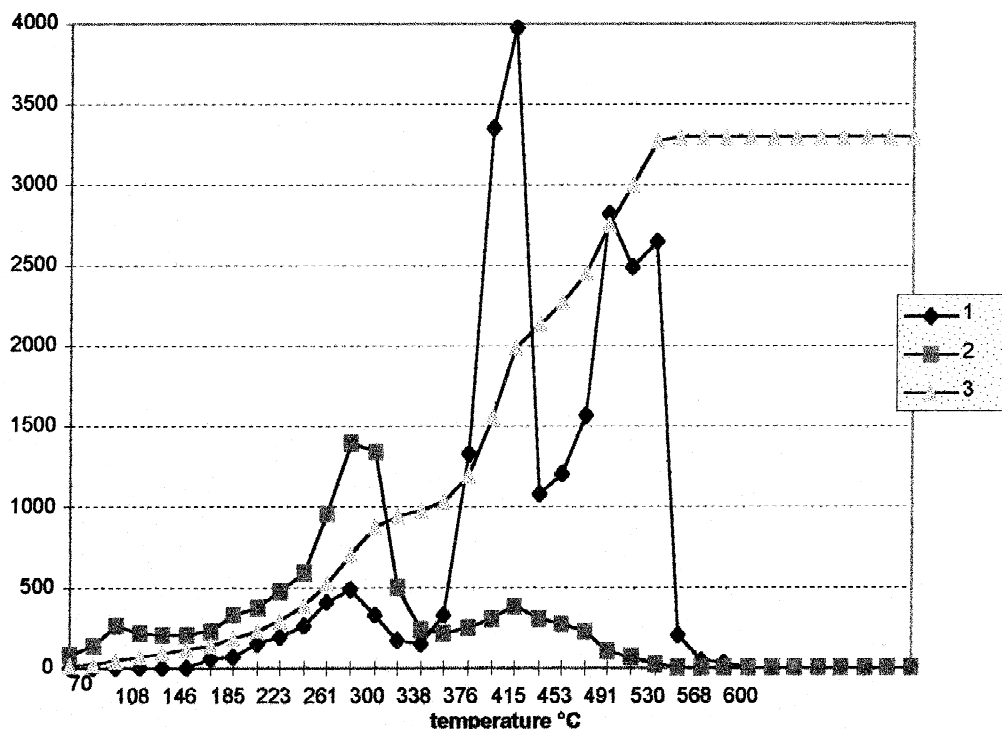


Fig. 5. Thermal decomposition of magnesium carbonate hydroxide: (1) $CO_2$; (2) $H_2O$; (3) total amount of evolved gases.

small portion of water are evolving in the range 350–450°C; (3) only $CO_2$ is evolving in the range 450–550°C. As ThGC permits one to follow the evolution of gaseous products independently, it is possible to measure the amounts of a given gas at distinct temperature intervals. In this way, it was found that five parts of water evolve during the first step and one part of water during the second step. This corresponds to the water of hydration (five molecules) and hydroxide (one group). The evolution of $CO_2$ occurs during steps two and three, suggesting that there are different structures at different stages and that these influence the undergoing decomposition at each stage. Apparently equal parts of carbonate degrade at these steps. These data could be interpreted as being due to the following reactions occurring in the sample
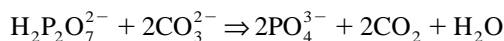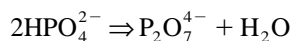
- dehydration (220–335°C)
- dehydroxylation and partial degradation of carbonate (350–450°C)
- degradation of carbonate (450–550°C)

Eventually, it can be seen that the process of degradation of carbonate is divided into two separate steps and can be caused by changes in the crystal structure of the salt during the dehydroxylation reaction.

### 3.2. Decomposition of apatites

As carbonate apatites have more complicated structures than the above salts, one would expect that the thermally induced changes in synthetic carbonate apatites are rather complex, involving overlapping reactions with release of several gaseous species. Their behavior on heating depends very much on the composition of apatite and on the way that it was synthesised. Using ThGC equipment, it was possible to cover the main temperature regions up to 600°C where evolution of gases take place. The main products evolved during the heating of precipitated apatites are water and carbon dioxide, as well as ammonia.

The water that evolves on the thermal treatment of synthesized apatites is of three different origins: adsorbed water, structurally incorporated water and water evolving as a result of interactions of the apatite constituents [10]:

$$2HPO_4^{2-} \Rightarrow P_2O_7^{4-} + H_2O$$

$$2NH_4^+ + 2HPO_4^{2-} \Rightarrow 2NH_3 + H_2O + H_2P_2O_7^{2-}$$

$$H_2P_2O_7^{2-} + 2CO_3^{2-} \Rightarrow 2PO_4^{3-} + 2CO_2 + H_2O$$

The adsorbed water is lost at 100–160°C for all samples (Fig. 6A). The evolution of the constitutional water from fluorcarbonate apatite lacking substitutions in the cationic site of the structure (sample 1) occurs over a wide temperature interval, up to 500°C, with a maximum at 300–320°C. In substituted magnesium carbonate apatite (sample 2), due to weakening of the crystal structure, the evolution of constitutional water proceeds at lower temperatures, with a maximum at about 200°C, which is more than 150°C lower than in the case of calcium apatites. The loss of water resulting from the reactions presented above also proceeds in the temperature range up to 600°C; the water loss was 2.1–2.8% for Ca-apatites and 8.3–10.2% for Mg-substituted apatites. Loss of $CO_2$ on heating carbonate apatites, which was investigated by GC and FTIR analysis of evolved gases, occurs between 450 and 950°C, with two or three maxima [10,13,14]. Following ThGC of the flourocarbonate apatite (sample 1), there is a slight loss of $CO_2$ that is caused by heating (up to 600°C), accounting for 13% of its total content. The slight rise in $CO_2$ concentration in the evolved gases at the temperatures of volatilization of constitutional water (300–500°C) indicate the release of retained $CO_2$. In contrast, the evolution of $CO_2$ from magnesium-substituted carbonate apatite proceeds at lower temperatures and to a greater extent; up to 72% of the theoretical content, with a maximum at 580°C, for fluorine-containing apatites (sample 2) and 30% of theoretical content with a maximum at 590°C for hydroxyapatite (sample 4) (Fig. 6B). The low temperature release of $CO_2$ gives rise to thermally induced rearrangements in the apatite structure, leading to a more stable crystalline phase of fluorapatite.

The evolution of ammonia from magnesium–ammonium carbonate apatite (sample 3) proceeds in ThGC experiments in the temperature interval 220–300°C what means the missing of adsorbed ammonia and the evolving of ammonia is as on heating of $MgNH_4PO_4$ (Fig. 4). The possibility of the existence
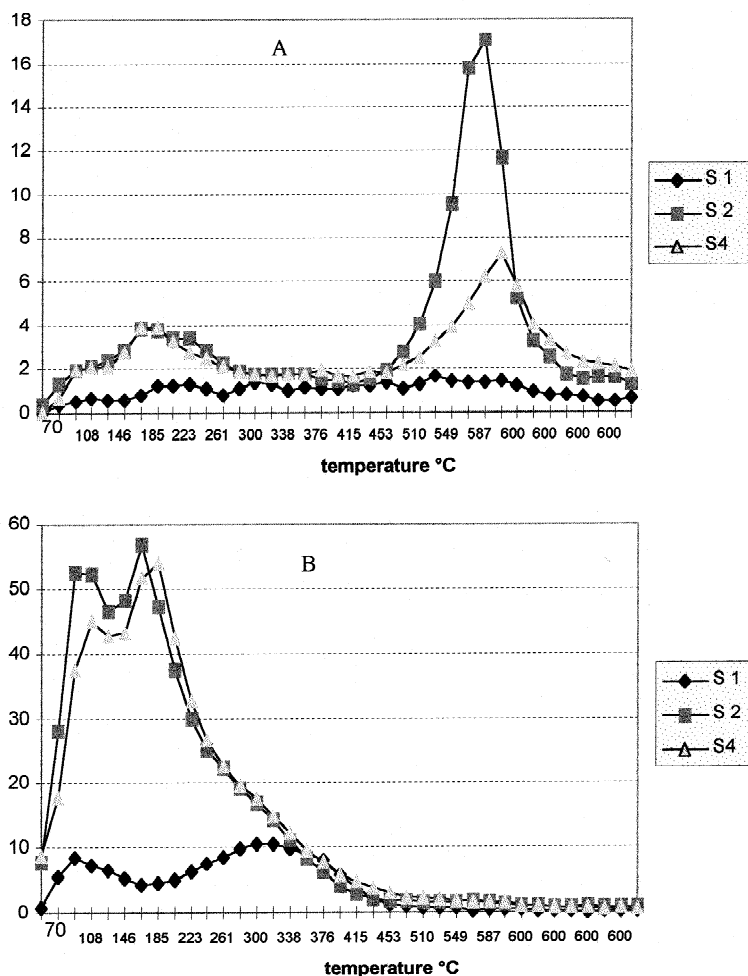
Fig. 6. Evolving of gases from the precipitated apatites: sample 1 (S1), sample 2 (S2) and sample 4 (S4): (A) evolution of $CO_2$; (B) evolution of $H_2O$.

of $MgNH_4PO_4$ as a separate phase in sample 3 is not excluded.

### 3.3. Reproducibility

To investigate the reproducibility of the proposed method, the calcium oxalate was analysed several times. The reproducibility of retention times can be estimated from one run consisting of 37 different chromatograms and, from this set, chromatograms where certain peaks appear were taken. In the case of calcium oxalate, these are the CO and $H_2O$ peaks. The data are presented in Table 1. As can be seen, the relative standard deviation (R.S.D.) of the re-

Table 1
Reproducibility of retention time (s) in a single experiment

| Run number | $H_2O$ | CO |
|---|---|---|
| 1 | 62.44 | 44.47 |
| 2 | 61.99 | 44.47 |
| 3 | 61.99 | 44.47 |
| 4 | 61.54 | 44.47 |
| 5 | 61.09 | 44.47 |
| 6 | 61.09 | 44.02 |
| 7 | 61.99 | 44.47 |
| Mean | 61.73 | 44.42 |
| SD | 0.510 | 0.254 |
| R.S.D. (%) | 0.8 | 0.6 |

Table 2
Reproducibility of retention times (s) and peak highs (counts/mass) over different experiments

| Run number | CO | | $H_2O$ | |
| --- | --- | --- | --- | --- |
| | Retention time | Peak height | Retention time | Peak height |
| 1 | 45.97 | 790 | 66.19 | 176 |
| 2 | 44.7 | 804 | 65.67 | 193 |
| 3 | 45.37 | 794 | 67.4 | 172 |
| 4 | 44.58 | 1017 | 65.49 | 209 |
| 5 | 45.55 | 721 | 67.87 | 171 |
| 6 | 45.09 | 863 | 66.56 | 222 |
| Mean | 45.21 | 800 | 66.53 | 197 |
| SD | 0.527 | 109 | 0.947 | 30 |
| R.S.D. (%) | 1.2 | 14 | 1.4 | 15 |

tention time is acceptable. Different runs were used for establishing the reproducibility of absolute peak heights and the long-term reproducibility of the retention times. The data are presented in Table 2. The peak height data did not show such good reproducibility. The high R.S.D. values for the peak height arise from the differences in the amount of sample weighed into the vial and possible differences in the temperature programs.

## 4. Conclusion

ThGC can be successfully used to obtain information on the composition and thermal stability of carbonate apatites. The lower temperature (up to 150°C) ranges reveal information about adsorbed gases and water of hydration. The evolution of gases at higher temperatures are more related to structural changes and decomposition of the samples. The components of an evolved gas mixture can be separated and identified easily. Evolved gas analysis by ThGC provides additional information to that which might be apparent by solid-state analysis alone, and this system is simple and versatile.

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