

THERMOCHROMATOGRAPHY OF INORGANIC SALTS

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Abstract. Results of thermal analysis of inorganic salts done to establish the potential utility of thermochromatography for this kind of experiment, are reported. The model samples chosen were calcium oxalate, ammonium oxalate, ammonium metavanadate, magnesium carbonate hydroxide, and magnesium ammonium phosphate hexahydrate. Each of these salts showed different thermal behaviour with several steps of degradation and simultaneous evolution of different gases. It is possible to describe the degradation reactions for each salt studied using the main separated and identified products that evolved (CO, CO₂, NH₃, H₂O).

Key words: evolved gas analysis, thermal analysis, gas chromatography, inorganic compounds.

INTRODUCTION

Thermochromatography (ThGC) [1] is an analysis method that combines thermal analysis and gas chromatography. The combination is achieved by the heating of a sample over time with a controlled temperature gradient while automatically sampling the head-space at predetermined reactor temperatures and injecting the samples into a gas chromatograph. Operationally, ThGC can be defined as temperature-programmed pyrolysis coupled with time-resolved, rapid gas chromatographic analysis of volatile products. The method has been used successfully in the analysis of different organic materials (polymers [2], fibres [3], oil shale [4]). Investigation of inorganic materials has moved to the fore of our interests because of the potential for ready construction of the mass-loss curve in terms of all detected volatile products. This could provide significant chemical insight into materials analysis and evolved gas studies. The study reported here uses model, inorganic salts whose thermal chemistry is known or thought to be known as a demonstration of the use of ThGC in such systems.

EXPERIMENTAL

The thermochromatographic analyser was constructed from an ordinary gas chromatograph by replacing the injector with a temperature programmable reactor and adding an automatic sampling system. The samples were placed in a flow-through, thermal-degradation reactor with dimensions 20 mm × 5 mm i.d. The evolving gases were swept from the reactor by the carrier gas passing first through a Deans'-type pneumatic sampling valve to the vent. The valve sampled the evolved products onto a capillary column located in the Carlo Erba 4200 gas chromatograph equipped with a Mod.450 HWD detector.

An Apple II computer controlled the evolving gas sampling and data collection activities. When a measurement run was completed, the data were transferred to a '486'-type PC for final calculation and display. All interfaces and control software were locally made and are detailed elsewhere [1]. A schematic of the analyser is given in Fig. 1. The thermal decomposition of all samples was

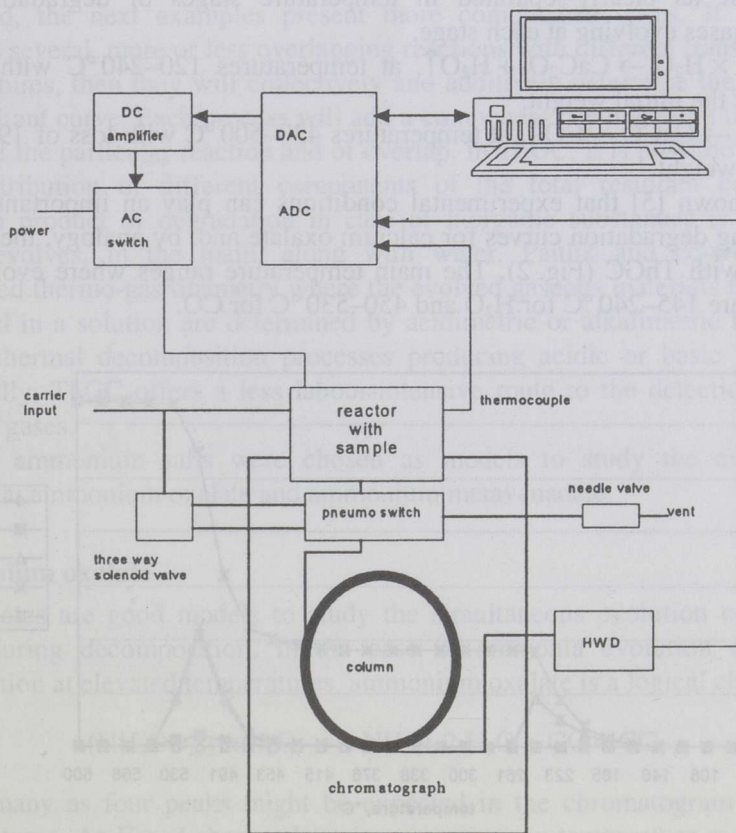


Fig. 1. Schematic of the thermochromatograph.

studied over the temperature interval 70–600 °C at a heating rate of 10 °C/min in inert atmosphere (He). The chromatographic column (NSW-PLOT HNU Nordion, Finland) was chosen to separate the main evolved products (CO, CO₂, NH₃, H₂O). The column temperature was kept at 70 °C and the detector temperature at 120 °C.

The following substances were studied: calcium oxalate, ammonium oxalate, ammonium metavanadate, magnesium carbonate hydroxide, and magnesium ammonium phosphate hexahydrate. The choice of the salts was a result of a desire to begin studies of apatites for which calibration of the thermo-chromatograph was needed.

RESULTS AND DISCUSSION

Calcium oxalate

Calcium oxalate is the most widely studied substance in thermal analysis because of its clearly-separated in temperature stages of degradation with different gases evolving at each stage.

1. $\text{CaC}_2\text{O}_4 \times \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}\uparrow$, at temperatures 120–240 °C with loss of 12.33% of the initial weight.
2. $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}\uparrow$, at temperatures 430–500 °C with loss of 19.18% of the initial weight.

It is known [5] that experimental conditions can play an important role in establishing degradation curves for calcium oxalate and, by analogy, the same is expected with ThGC (Fig. 2). The main temperature ranges where evolution is observed are 145–240 °C for H₂O and 450–530 °C for CO.

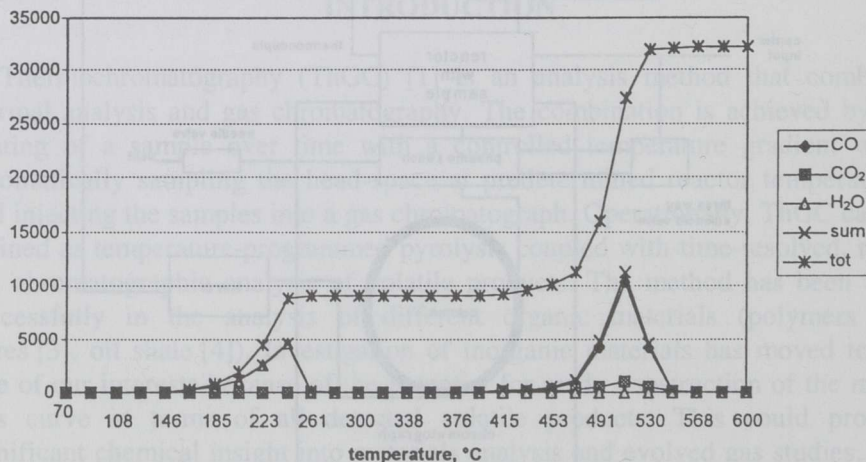
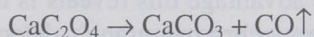
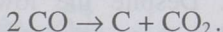


Fig. 2. Thermal decomposition of calcium oxalate: CO, evolving of carbon oxide; CO₂, evolving of carbon dioxide; H₂O, evolving of water; sum, summarized evolving of all products; tot, cumulative evolving of all products.

A significant feature, not seen with thermogravimetric analysis, was observed with ThGC in the second stage of degradation. Chromatography of evolved products shows co-evolution of CO₂ and CO in what could be explained as disproportionation of CO into CO₂ and C. That possibility is supported by the black, carbon-like colour of the sample after heating. This suggests that there are two reactions at the second temperature range:



and



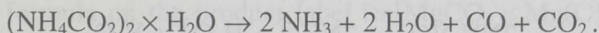
It is known [6] that in the case of barium oxalate hemi-hydrate decomposition in an N₂ atmosphere C is formed and that in the thermolysis of calcium oxalate to calcium carbonate in vacuum about 47% of the CO disproportionates into CO₂ and C. In our case, the fraction of CO involved in this kind of secondary reaction was approximately 30%.

While in case of calcium oxalate the fractional degradation processes are well separated, the next examples present more complicated cases. If a process involves several, more or less overlapping reactions with different transformation temperatures, then they will collectively and additively determine the course of the resultant curve. Each process will add a component dependent on the relative extent of the particular reaction and of overlap. In ThGC, it is possible to resolve the contribution of different components of the total resultant curve. One common product of degradation in case of inorganic substances is ammonia, which evolves, in the main, along with water. Paulik and co-workers [7] developed thermo-gas titrimetry where the evolved gaseous materials that can be adsorbed in a solution are determined by acidimetric or alkalimetric titration to follow thermal decomposition processes producing acidic or basic gas-phase. Potentially, ThGC offers a less labour-intensive route to the detection of such evolved gases.

Two ammonium salts were chosen as models to study the evolving of ammonia: ammonium oxalate and ammonium metavanadate.

Ammonium oxalate

Oxalates are good models to study the simultaneous evolution of different gases during decomposition. In the case of ammonia evolution during the degradation at elevated temperatures, ammonium oxalate is a logical choice:



As many as four peaks might be expected in the chromatogram at certain temperatures. As Fig. 3 shows, there is a very narrow temperature region (200–240 °C) over which degradation begins and the substance degrades completely. In our experiment, the thermal resolution was 19 °C. This is obviously too broad

in the case of fast processes such as is the case here. Differences in peak heights in Fig. 3 are attributed to different detector response factors for the individual evolved gases. The water evolving at 108 °C is a result of the desorption of hygroscopically associated water and for quantitative degradation estimates, the salt must be dried at 105 °C before the degradation experiment is begun. The amounts of volatile products measured by ThGC experiments confirm the above-given reaction scheme. The advantage this reveals is that ammonium oxalate can be used to calibrate the thermochromatograph's detector in one run for several, different and common gases. Despite the low temperature resolution, the advantage of ThGC is revealed in these cases permitting separate determination of the different decomposition products that are formed concurrently.

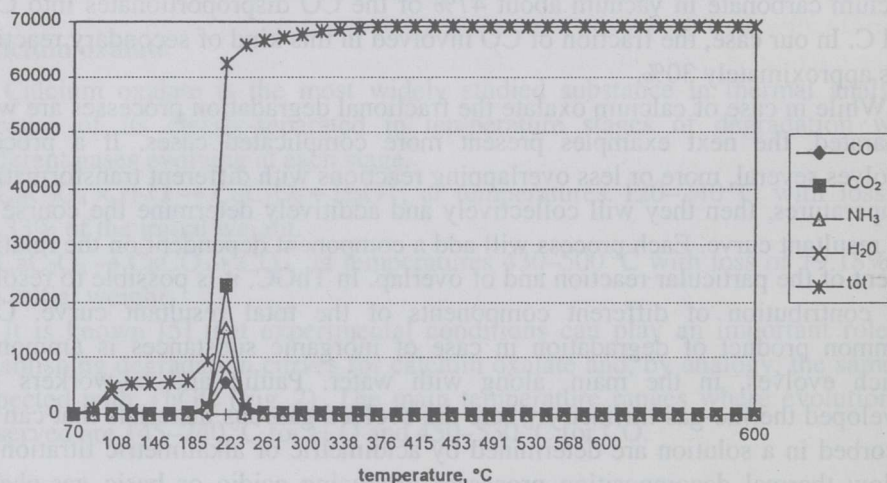
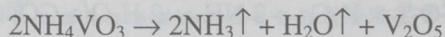


Fig. 3. Thermal decomposition of ammonium oxalate: CO, evolving of carbon oxide; CO₂, evolving of carbon dioxide; NH₃, evolving of ammonia; H₂O, evolving of water; tot, cumulative evolving of all products.

Ammonium metavanadate

Another model substance used for studying the evolving of ammonia upon heating is ammonium metavanadate. It is known that the thermal degradation of ammonium metavanadate takes place as follows:



and it should give two peaks on chromatogram in one temperature region. However, this assumption is in error and the situation is clearly more complex. The ThGC evolving gas curves (Fig. 4) reveal three maxima to follow. The first temperature region is 165–240 °C when water and ammonia are both evolving.

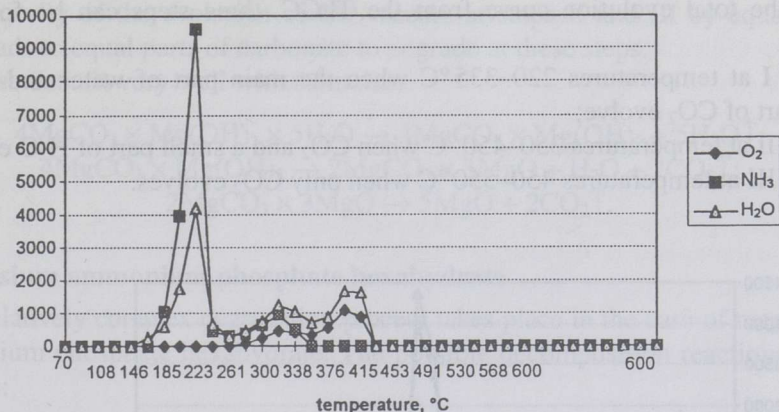
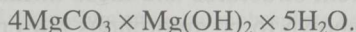


Fig. 4. Thermal decomposition of ammonium metavanadate: O₂, evolving of oxygen; NH₃, evolving of ammonia; H₂O, evolving of water.

This could be the degradation according to the formula above. In textbooks, the melting point of ammonium metavanadate is given at 200 °C but apparently melting is accompanied by degradation. There are two more, distinct temperature regions where gases evolve. This suggests that ammonium metavanadate is degrading only in part according to the formula given above. Weight loss during the experiment confirms this (22.2% according to the formula, while 27% was observed). There is a second temperature region (280–350 °C) where some amount of water and ammonia evolve and the third substance starts to evolve. The third and final temperature region where water and this third substance both evolve is 370–430 °C. This unknown substance is oxygen. All this suggests that the gases evolved influence the degradation of the melted salt. From the evolving of oxygen, it appears that in the second stage both reactions could take place. This rather surprising result is analogous with the decomposition of manganese dioxides which show (a) water loss, (b) dehydroxylation, and finally (c) oxygen release [8].

Hydromagnesite

A more complicated pattern of degradation products is seen in case of hydromagnesite. This compound belongs to a group of aquoxides with complex crystal structures for which multistage decomposition is usually observed. There was no exact formula on the product label ($m[\text{MgCO}_3 \times \text{Mg}(\text{OH})_2] \times n\text{H}_2\text{O}$). It was thought that this could be a challenge for the technique of ThGC to determine the ‘right’ formula despite complications of this class of salts. The most widely spread magnesium carbonate hydroxide hydrate has the formula:



On the total evolution curve from the ThGC, three steps can be followed (Fig. 5):

Step I at temperatures 220–335 °C when the main part of water and only a small part of CO₂ evolve;

Step II at temperatures 350–450 °C when CO₂ and a small part of H₂O evolve;

Step III at temperatures 450–550 °C when only CO₂ evolves.

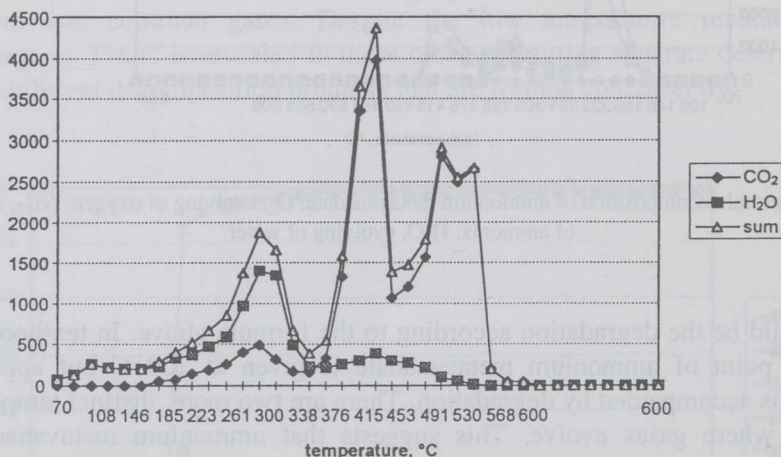


Fig. 5. Thermal degradation of hydromagnesite: CO₂, evolving of carbon dioxide; H₂O, evolving of water; sum, summarized evolving of all products.

In case of water, it is hard to decide whether the H₂O is coming from the H₂O of crystallization or from OH groups and what the individual steps of the decomposition actually signify. As the curves showed the thermal decomposition to be three-stage, it was concluded that the reactions proceeded consecutively with partial overlap. Based on these data, one can suggest processes related to each step:

Step I: dehydration;

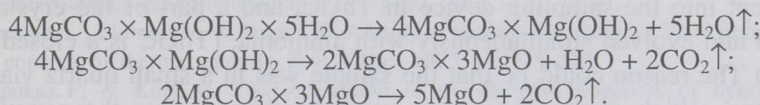
Step II: dehydroxilation and partly degradation of carbonate;

Step III: degradation of carbonate.

As ThGC permits one to follow the evolving of gaseous products independently then it is possible to measure the amounts of a given gas for given temperature intervals. It is clear from the amounts evolved that five parts of water evolves at step I and one part at step II. This confirms the amount of crystal water (five molecules) and hydroxide (one group). Evolving of CO₂ in different stages shows that there are different structures and these influence its degradation. The intermediate formed was shown to be amorphous but crystallizing at 500 °C [9].

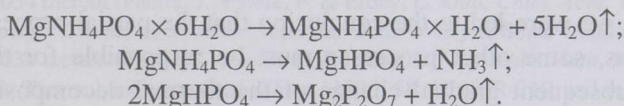
The majority of the evolution of CO_2 occurs at steps II and III by equal parts. This leads to equal parts of carbonate to degrade at these steps.

These data fit very well with formulas:



Magnesium ammonium phosphate hexahydrate

A relatively complex degradation process takes place in the case of magnesium ammonium phosphate hexahydrate. The possible decomposition reactions are as follows:



It was proved [10] that the course of the reactions depends on the experimental conditions of either open or closed headspace above the sample. In case of an open space above the material, the dehydration reactions cannot be seen separately whereas in case of a closed space, the evolving of crystal water is divided into two steps. It appears then that the entire degradation is composed of four partial processes. ThGC is a good tool to check this proposal. In the evolution curve from ThGC (Fig. 6) one can follow three peaks:

- (1) Temperature region 90–190 °C, when water is evolving (73.7% from the total amount);
- (2) Temperature region 240–320 °C, when water (17.8% from the total amount) and ammonia are evolving simultaneously;
- (3) A wide temperature region 450–570 °C, when water is evolving (3.2%).

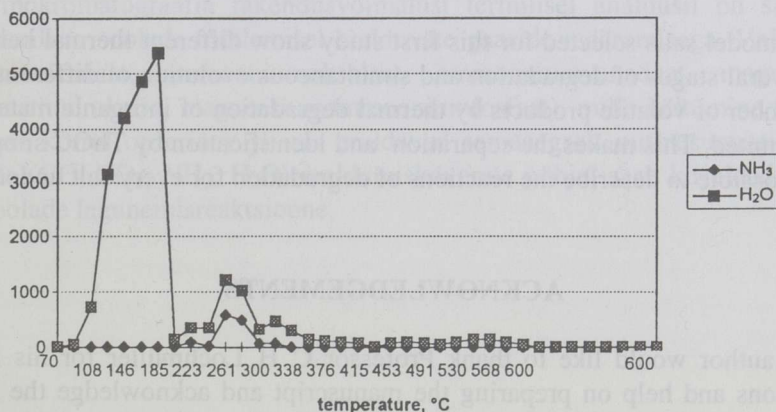
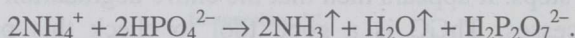


Fig. 6. Thermal degradation of magnesium ammonium phosphate hexahydrate: NH_3 , evolving of ammonia; H_2O , evolving of water.

These data indicate that the release of five water molecules and the decomposition of the intermediate $\text{MgNH}_4\text{PO}_4 \times \text{H}_2\text{O}$ became well separated although the sample was in flow through the reactor and the reaction products were swept into the sampling device in ThGC, and a part of the crystal water remained and evolved simultaneously with ammonia. (ThGC is a closed system analogy.) The reason could be that the sample was in a small quartz vial inside the reactor, which means there was some headspace over the sample. This evolution took place in the temperature region 240–320 °C and yielded MgHPO_4 . The third step at higher temperatures (450–570 °C) corresponds to the evolving of constitutional water. However, from the amounts of water evolving at different steps, it is clear that part of the constitutional water is evolving simultaneously with ammonia.

Eventually, we were led to the conclusion that the partial processes were not separated. Thus, some other processes must be responsible for the temporary ceasing and subsequent gradual change of the thermal decomposition and this could be a halt in the re-crystallization of the new phase [9].

From this thermal analysis of phosphate one could confirm the conclusion posited for synthetic apatites [11] and the evolving of ammonia, i.e. that there is no adsorbed ammonia and evolution is taking place at temperatures 275–280 °C according to the reaction



This is an excellent example where evolved gas analysis could be applied together with other thermoanalytical methods like differential scanning calorimetry and others to get a full description of the processes involved.

CONCLUSION

The model salts selected for this first study show different thermal behaviour with several stages of degradation and simultaneous evolution of different gases. The number of volatile products by thermal degradation of inorganic materials is rather limited. This makes the separation and identification by ThGC simple and it was possible to describe the reactions of degradation for every salt under study.

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ANORGAANILISTE SOOLADE TERMOKROMATOGRAAFIA

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Termokromatograafia rakendusvõimalusi termilisel analüüsil on selgitatud anorgaaniliste soolade töötlemisel eralduvate gaaside määramisega. Valiti ained (kaltsiumoksalaat, ammoniumoksalaat, ammoniumvanadaat, magneesium-karbonaathüdroksiid, magneesiumammooniumfosfaat), mille käitumine termilise mõjutuse korral on erinev ja mis eraldavad samaaegselt mitmesuguseid gaase. Gaaside (CO, CO₂, NH₃, H₂O) eraldumiskõverate põhjal saab kirjeldada uuritava soolade lagunemisreaktsioone.