AN APPARATUS FOR SIMULTANEOUS THERMAL ANALYSIS AND ITS APPLICATION IN GEOLOGICAL RESEARCH

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ABSTRACT

Combination of a home-made thermoanalytical device (Derivatograph, MOM) and a quadrupole mass spectrometer (QMS–D, ATOMKI) is presented, and the simultaneous thermoanalytical method (DTA, DTG, TG, QMS–EGA) has been successfully applied in many fields of mineralogy, petrology, geochemistry and chemostratigraphy.
In Hungary, positive experience has been obtained in the following fields:
— determination of rare mineral in the Carpathian Basin.
— Diagenetic and hydrothermal processes and facies were characterized by distinguished mineral associations in Hungary and Cuba.
— Geological dating by investigations of sporadic finds (bones) of Neogene vertebrates.

INTRODUCTION

The most important information on various evolved gas analytic methods, such as mass spectrometry, gas chromatography, infra-red absorption, selective sorption and thermogas titrimetry will be found in the books and in the well-known journals and monographs. The Proceedings of the ICTA and ESTA provide an up-to-date picture of the stage of development of MS and GC–MS coupling system and their applications (e.g. BRACEWELL and ROBERTSON 1980; FRIPIAT 1982; MORGAN 1977; MÜLLER—VONMOOS and MÜLLER 1974; PAULIK and PAULIK 1981; SZÉKELY *et al.* 1980; WARNE *et al.* 1985).
The new method was used parallelly with thermogas titrimetry (TGT) and IR, GC, X-ray analyses to determine composition of the inorganic and organic compounds, minerals, rocks, building and raw materials, and has been successfully applied in many fields of chemistry and geochemistry (DÉVAI *et al.* 1984; KOZÁK *et al.* 1985; SZÖŐR *et al.* 1984; SZÖŐR and BOHÁTKA 1985; SZÖŐR and BALÁZS 1988).
A few examples demonstrate that simultaneous technique is very helpful and it is basic method for wide area of experience.

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A home-made quadrupole mass spectometer (BERECZ *et al.* 1983) has been coupled to the Derivatograph and got a versatile instrument promising the possibility of a fast, sensitive evolved gas analysis (*Fig. 1.*).
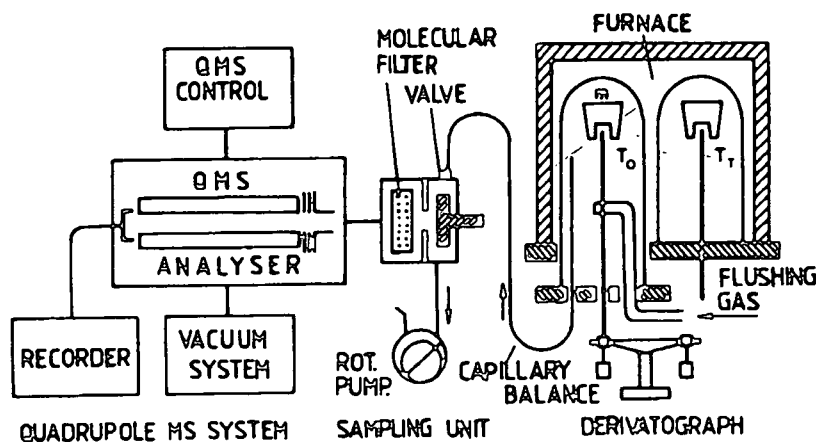

Fig. 1. Schematic drawing of the Derivatograph (MOM) and QMS-D (ATOMKI) system
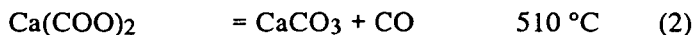
The quadrupole mass spectrometer has a mass range of 1–300 a.m.u. and a sensitivity of $4 \cdot 10^{-4}$ A/mbar with Faraday cup. It is mounted on a bakeable high vacuum system consisting of a liquid nitrogen cooled refrigerator, water cooled oil trap and oil diffusion pump. Ultimate pressure is less than $1 \cdot 10^{-8}$ mbar without baking. Gases are pumped from the reaction chamber through a 1.2 m long capillary and a small portion of the sample is introduced into the quadrupole via a molecular filter at the low-pressure end of the capillary. The tip of capillary is 2 cm below the sample holder. The coupling unit can be heated up to 200 °C, its gas consumption is about 0.5 cm^3/s, response time is 50 ms but this latter is not exploited because of the large volume of the reaction chamber (~50 cm^3).
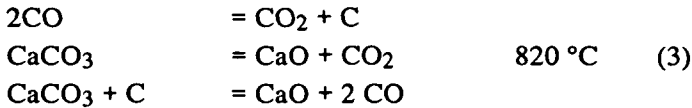
The response time of the whole coupled system is 20 s at 3 cm^3/s air flow rate. This is satisfactory as the fastest heating program of the Derivatograph is 20 °C/min. Sensitivity: during the thermoanalysis is 1 mg Ca(COO)$_2$ · H$_2$O, the signal at the output of the quadrupole is 50 times higher than the noise amplitude. The volatile components are identified on the basis of the complete mass-spectra, while the changes in each component of given mass are monitored as a function of temperature with the aid if a peak selector.

The measurements were performed under the following conditions: temperature range 1000 °C; rate of heating: 10 °C /minute in helium or air current; sample holder: platinum or ceramic crucibles.

The interpretation of calcium oxalate monohydrate (whewellite) an example of our first investigations (*Fig. 2*).

The decomposition processes take places as follow in helium atmosphere.

$$Ca(COO)_2 \cdot H_2O = Ca(COO)_2 + H_2O \quad 210 \,°C \quad (1)$$
$$Ca(COO)_2 \quad = CaCO_3 + CO \quad 510 \,°C \quad (2)$$

$$2CO \qquad = CO_2 + C$$
$$CaCO_3 \qquad = CaO + CO_2 \qquad 820\ °C \qquad (3)$$
$$CaCO_3 + C \qquad = CaO + 2\ CO$$

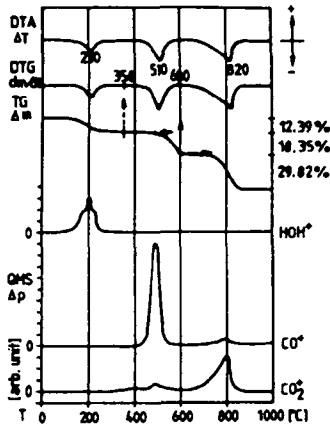The processes are different in air atmosphere.

Fig. 2. The thermal decomposition of whewellite

RESULTS AND DISCUSSIONS

The examples reported in this paper demonstrate that simultaneous technique is a very helpful means in the characterization of geological materials.

Mellite, hydrate aluminium mellate, $Al_2[C_{12}O_{12}]\cdot$ 18 or 16 (?) H_2O is a very rare mineral, it is unique in the Carpathian Basin (Csordakút, Hungary). The crystal water content of mellite was controversial up to the present. The *Fig. 3.* shows the loss of water in the first endothermic process, it is 39.73 %, ~16 moles in the formula (SZÖÖR and BOHÁTKA 1985).
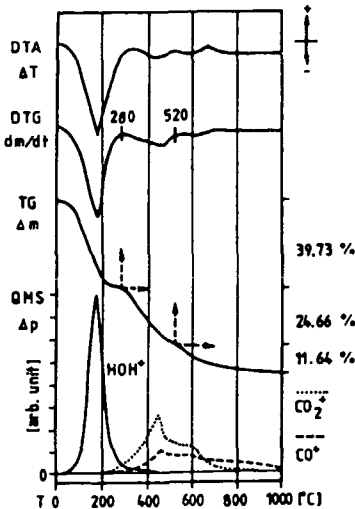

Fig. 3. The thermal decomposition of mellite

A Lower Pannonian (Miocene) gravel complex is cemented by marcasite deposited by low temperature hydrothermal activity (VICZIÁN *et al.* 1986). In this locality the light yellow incrustation on the weathered rock surface were hydrous iron sulphate minerals. The X-ray diffraction indicated the minerals as copiapite, $(Fe^{2+}, Mg)Fe_4^{3+}[(OH)(SO_4)_3]_2 \cdot 20H_2O$ and rhomboclase, $Fe^{3+}H[SO_4]_2 \cdot 4H_2O$. The combined thermoanalytical investigations showed H_2O and SO_2 as main components, minor amounts of S and CO_2 indicated impurities in the evolved gases (*Fig. 4.*).
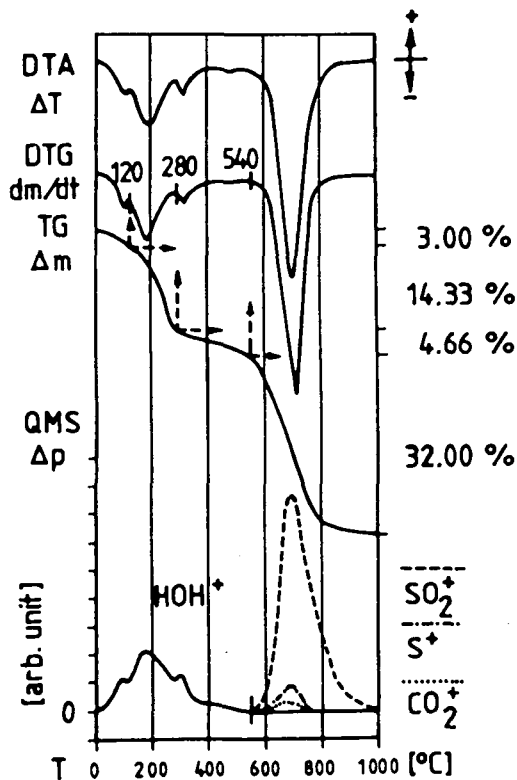

Fig. 4. The thermal decomposition of mixture copiapite and rhomboclase

The percentages of the hydrous sulphate minerals are copiapite: 54 percent, rhomboclase: 23 percent as computed considering the weight loss of H_2O and SO_3 from the total sample. The remaining 23 percent is mainly amorphous SiO_2.

This method was used to determine silicate, carbonate, hydroxide mineral paragenesis of ultramafic rocks (peridotite, serpentinite). According to the water and carbon dioxide detected to antigorite, chrysotile, brucite and magnezito-calcite were identified (*Fig. 5.*).

The mass spectrometry combined with Derivatograph can reveal the presence of various carbonates, sulphates, clay minerals in raw and building materials. *Fig. 6.* shows two typical examples.

At the foreground of North Borsod Karst, Hungary, there are some shallow boreholes, which have organic material bearing layers in the Upper Pannonian ingression lagoon sediments. Two characteristic diagenetic processes and facies
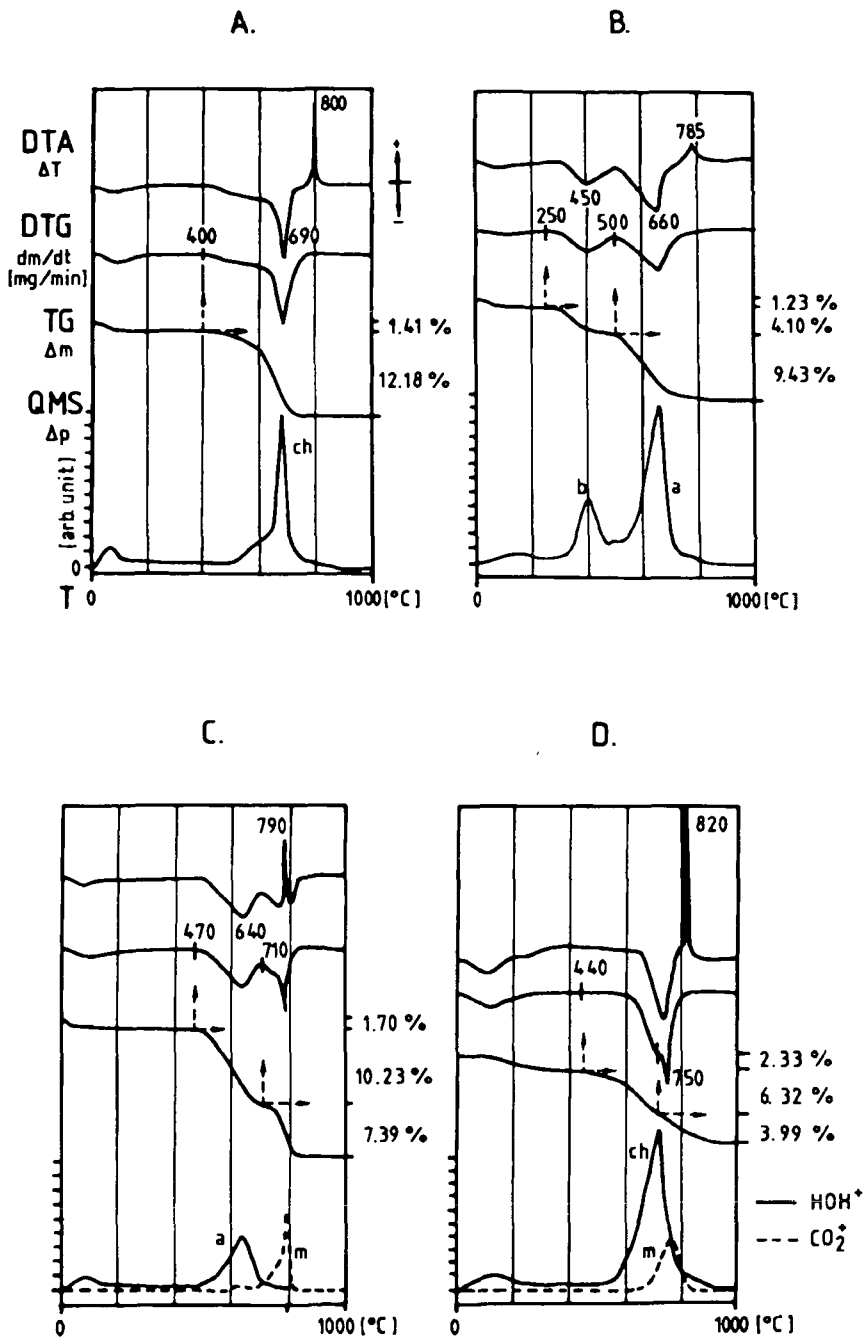
Fig. 5. Mineral paragenesis of serpentinite, from Bogoslovac, Yugoslavia (A), Trodos, Cyprus (B), Bódvarakó, Hungary (C) and Tacajo, Cuba (D)
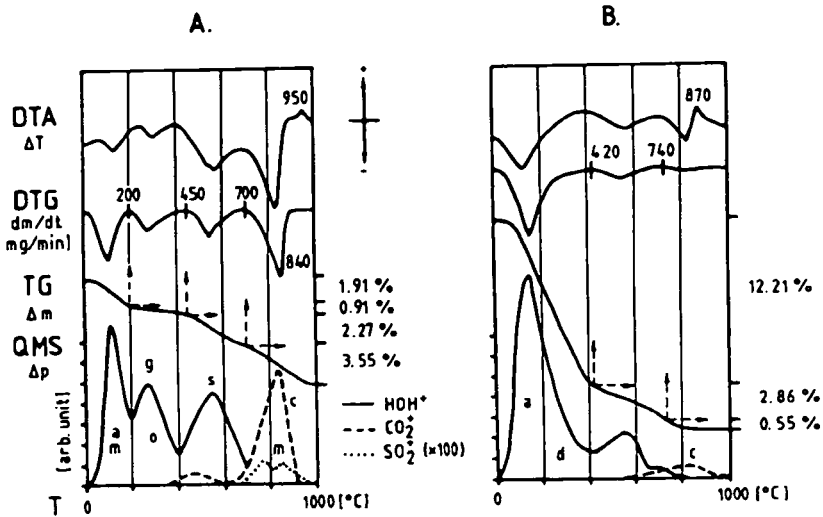a=antigorite, ch=chrysotile, b=brucite, m=magnesito-calcite

Fig. 6. Mineral paragenesis of a brick clay from Great Hungarian Plain (A) and an important tuffigene raw material, beidellite from Banes, Cuba (B)
a=amorphous material, c=calcite, d=dioctahedral smectite, g=goethite, m=mirabilite, s=interstratified mica-smectite, o=organic material

were distinguished by DTA, DTG, TG, QMS-EGA, GC, IR and Rock Eval pyrolysis methods (SZÖÖR *et al.* 1986). In the siderite facies, the organic materials was disintegrated under oxidative circumstances, while in the case of calcite and gel pyrite facies, typical aliphatic protobitumens accumulated in a reductive environment (*Fig. 7.*).

A new geochronological method has been developed by the authors (SZÖÖR, 1982a,b; SZÖÖR *et al.* 1987). The evaluation of the DTA, DTG, TG curves of Quaternary vertebrate fossil materials produced characteristic parameters closely related to geological age. Using this statement as a means for dating carried out a chronostratigraphic evaluation.

In this paper we demonstrate the mass spectrometric thermal analysis which provided the required information to explain the difference in the composition of fossil bones by measuring the evolved gases.

In the course of our work this chronological well-defined sporadic find was evaluated. The first data is 20100 years, the other one is 100000 years. *Fig. 8.* shows the results of examinations. Water as basic constituent was released up to 220 °C from the organic and inorganic structures (A process). In this range carbon dioxide relates to the beginning of the decomposition of fossile collagen. The main process B takes place between 220 and 600 °C. The quantity and MS-pattern of organic gas components are different in samples of different ages. The carbonate of apatite and calcite secondarily built into the structure dissociated in the range of 600—1000 °C (C process).

In the future it will be completed to reveal the regularities of collagene with check by GC-MS analyses.
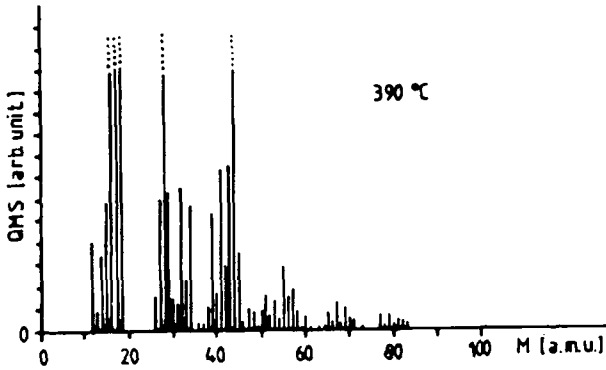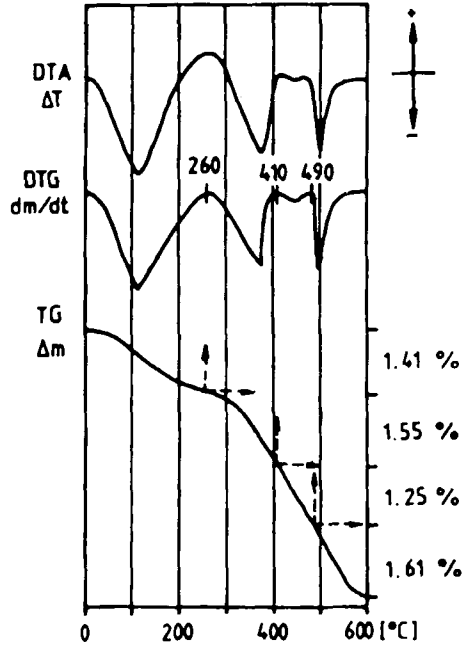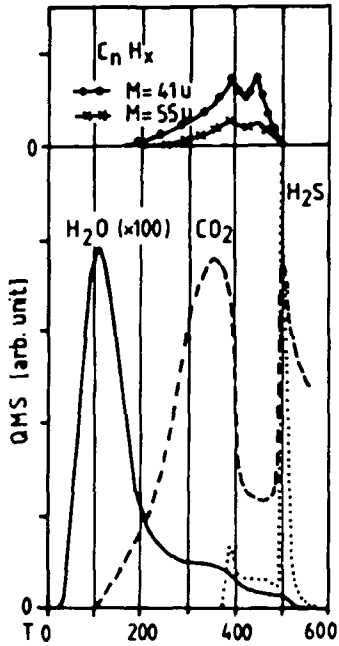
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Fig. 7. DTA, DTG, TG, QMS-EGA analysis of argillaceous aleurite ("oil shale")from Teresztenye, Hungary. H_2O, CO_2, H_2S, mass number (M) 41 and 55 were continuously detected, complete mass spectrum at 390 °C (in He-atmosphere with some air-contamination)
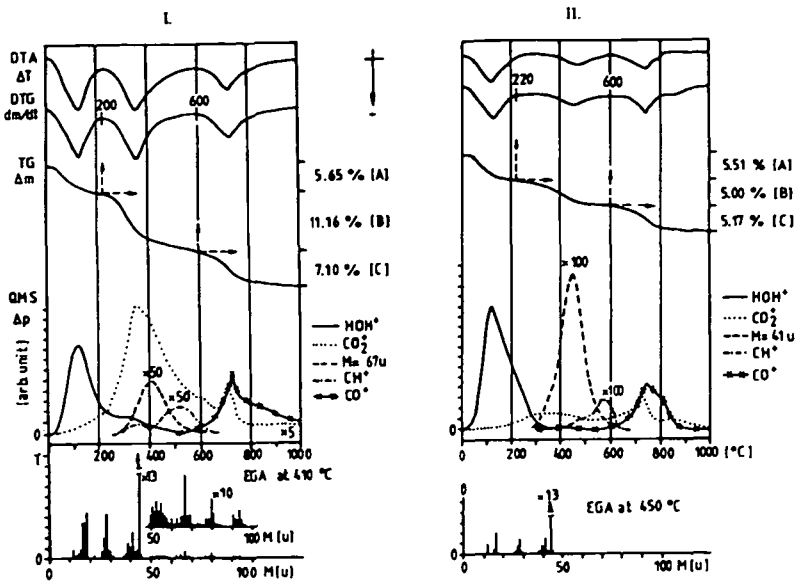
Fig. 8. DTA, DTG, TG, QMS-EGA analysis of sporadic finds (bones)
I.=20000 and II.=100000 years old (B.P.)

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