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DERIVATOGRAPH-QMS SYSTEM IN GEOCHEMICAL RESEARCH

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ABSTRACT

A quadrupole mass spectrometer /ATOMKI, Hungary/ is coupled to a Derivatograph /MOM, Hungary/. The complex thermoanalytical method has been successfully applied in many fields of mineralogy, petrology and geochemistry. Some examples of the combined analysis are shown.

INTRODUCTION

A quadrupole mass spectrometer /QMS/ [1,2] has been coupled to a Derivatograph [3]. The QMS makes possible to carry out complex and sensitive evolved gas analysis EGA simultaneously with the TG, DTG and DTA analyses by the well known thermoanalytical instrument. This combined method was used parallel with the conventional TGT-EGA technique [4] to determine carbonate, sulphate, clay mineral and organic content of rocks and building materials [2, 5] .

METHOD

The instruments used in the experiments: Derivatograph-1000 ^{o}C /MOM, Hungary/, quadrupole mass spectrometer, type QMS-300 /ATOMKI, Hungary/ and a dynamic sampling system /ATOMKI/. Samples were placed in platinum crucibles. 200 l/s He flow was maintained to establish the inert atmosphere for dynamic sampling. Al_2O_3 was used as inert reference and the heating rate was 10 ^{o}C/min.

The evolved gases were pumped from the furnace through a 1.2 m long capillary and a small portion was introduced into the quadrupole via a molecular filter at the low-pressure end of the capillary. The coupling unit can be heated up to 200 ^{o}C, its gas consumption is about 0.5 ml/s, response time is 50 ms. The QMS has a mass

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range of 1-300 amu and a sensitivity of $4 \cdot 10^{-4}$ A/mbar with Faraday cup. Ultimate pressure is less than $1 \cdot 10^{-8}$ mbar without baking.

RESULTS

The Pleistocene fluviatile gravel complex at Uzsa /NE part of the Keszthely Mts., Hungary/ is cemented by marcasite deposited by low temperature hydrothermal activity. In this locality the vivid yellow incrustrations on the weathered rock surfaces were hydrous iron sulphate minerals. The X-ray diffraction [6] using the standard data of the ICPDS cards no. 20-659 and 27-245 indicated the minerals as copiapite $(MG_{0.59}Al_{0.30})\ (Fe^{3+}_{3.56}Al_{0.44})\ (SO_4)_6\ (OH)_2 \cdot 19.7\ H_2O$ and rhomboclase $FeH[SO_4]_2 \cdot 4\ H_2O$. The combined thermoanalytical investigations showed H_2O and SO_2 as main components /Fig.1/. Minor amounts of S and CO_2 indicated

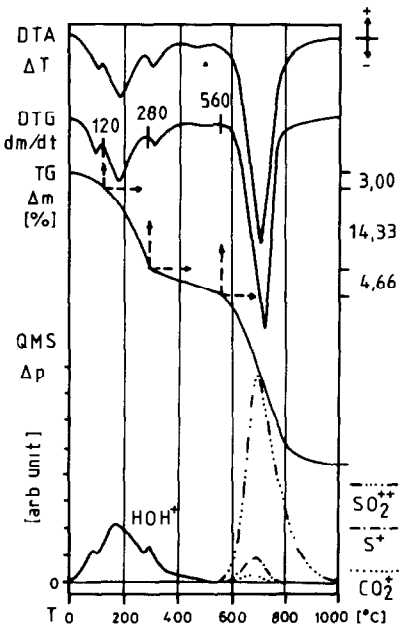

Fig.1. DTA, DTG, TG and QMS-EGA curves of a mixture of copiapite and rhomboclase

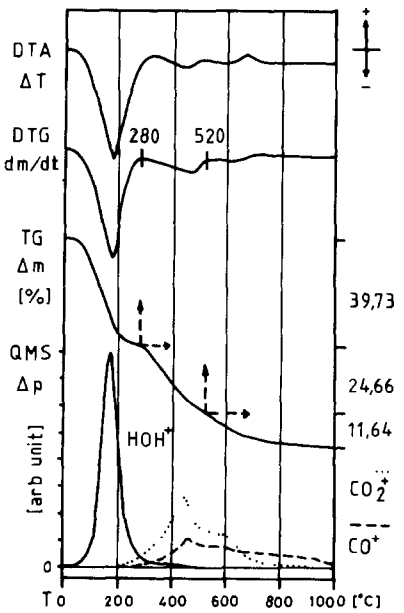

Fig.2. DTA, DTG, TG and QMS-EGA curves of mellite

impurities in the evolved gases. The calculated weight ratio of H_2O and SO_3 verified the ratio of copiapite and rhomboclase suggested by X-ray diffraction. This is the first known occurence of rhomboclase and the second one of copiapite in the present day territory of Hungary.

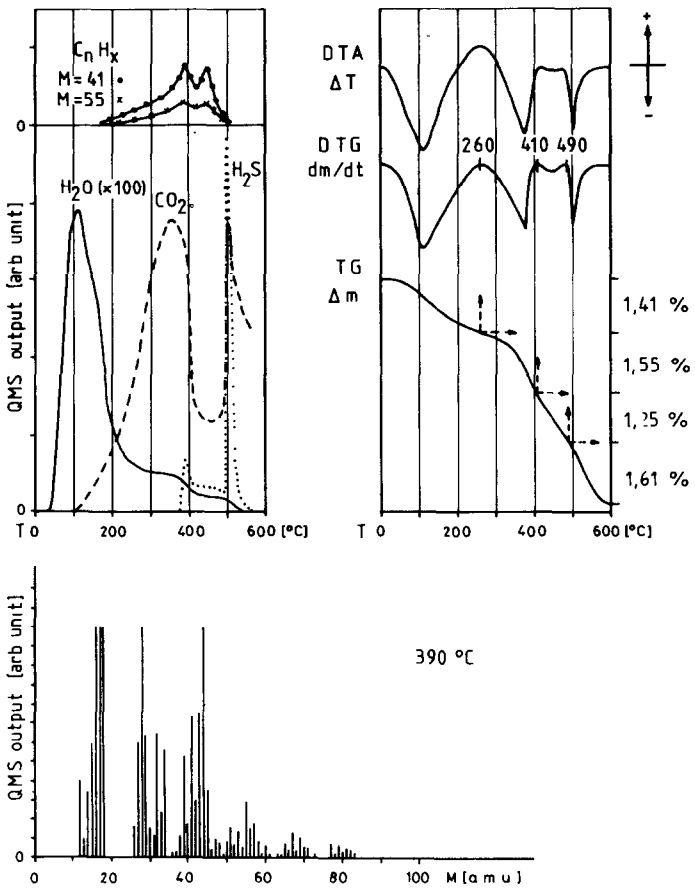

Fig.3. Thermoanalytical and QMS-EGA analysis of oil shale from Teresztenye-2/11. borehole, 48.25 m. $H_2O/18/$, $CO_2/44/$, $H_2S/34/$ and mass numbers 41,66 were continously detected. A complete mass spectrum was recorded at 390 ^{o}C /N_2, O_2, Ar are impurities in the He carrier gas/.

Mellite /hydrated aluminium mellate, $Al_2[C_{12}O_{12}]\cdot 18$ /?/ H_2O or 16 /?/ H_2O/ is a very rare mineral. It is unique in the Carpatic Basin and occures in Eocene brown coal desposit of Csordakut, Transdanubia, Hungary [7]. The crystal water content of mellite was controversial up to the present. According to our DTA, DTG, TG and QMS-EGA records /Fig.2/ the loss of water in the first endothermic process is 39,73 %~16 moles in the formula.

At the foreground of North Borsod-Karst, Hungary /Teresztenye and Szőlősardó villages/ there are some shallow boreholes, wich have oil shale layers in the Upper Pannonian ingression lagoon sediments. Two characteristic diagenetic processes and facies were distinguished by instrumental investigations /thermoanalysis, gas chromatography, Ir spectroscopy/. In the siderite facies the organic material was decomposed under oxydative circumstances, while in the case of calcite and gel pyrite facies typical aliphatic protobitumens accumulated in reductive environment produced oil shale /Fig.3/.

CONCLUSION

The examples reported in this paper demonstrate that simultaneous TG, DTG, DTA and QMS-EGA technique is a very helpful means in the characterization of geological materials, it is a basic method for geochemical research.

The QMS completes the Derivatograph in this combination: it identifies the evolved inorganic and organic gas products, helps in DTG and TG evaluation and fairly fast compared to the thermoprocesses.

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