Thermochimica Acta, 20 (1977) 387–393

DTA–TG–MS IN THE INVESTIGATION OF CLAYS

QUANTITATIVE DETERMINATION OF H_2O, CO AND CO_2 BY EVOLVED GAS ANALYSIS WITH A MASS SPECTROMETER

MAX MÜLLER-VONMOOS, GÜNTER KAHR AND ANTON RUB
Institute for Crystallography and Petrography and Institute for Foundation Engineering and Soil Mechanics, Swiss Federal Institute of Technology, CH-8006 Zurich (Switzerland)
(Received 20 October 1976)

ABSTRACT

A thermoanalyzer (Mettler) combined with a quadrupole mass spectrometer (Balzers) by a capillary inlet system allows simultaneous DTA, TG and evolved gas analysis in different atmospheres. Decomposition of $CaC_2O_4 \cdot H_2O$ in air and argon, respectively, demonstrates the usefulness of the mass spectrometer for the quantitative determination of H_2O, CO_2 and CO. Decomposition of $NaHCO_3$ at a heating rate of 10°C min^{-1} reveals that H_2O and CO_2 evolved simultaneously at a relatively low temperature (159°C) can also be determined quantitatively and nearly without retardation compared with the weight loss step. In the investigation of clays an example will be given of the usefulness of the described DTA–TG–MS in the quantitative interpretation of overlapping reactions.

INTRODUCTION

Most natural clays have a complex mineralogical composition. Interpretation of DTA of such clays may be difficult because of overlapping reactions and alterations in reactions typical of a certain mineral caused by solid state reactions[1]. Today, therefore, it is common practice to combine DTA with other methods such as TG, X-ray, IR and evolved gas analysis. For the investigations presented in this paper, we used a thermoanalyzer (Mettler) in combination with a quadrupole mass spectrometer (Balzers)[2]. In an attempt to determine the mineralogical composition of clays and their organic content quantitatively by thermal analysis, we started the investigations presented in this paper by clarifying how accurately H_2O, CO and CO_2 can be determined quantitatively by evolved gas analysis with a mass spectrometer.

METHOD

A thermoanalyzer (Mettler) was connected to a quadrupole mass spectrometer (Balzers) by an inlet system (Fig. 1). The samples were heated in platinum crucibles

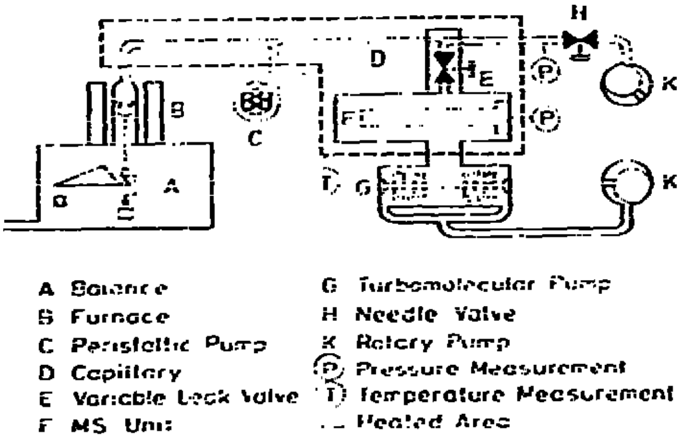


Fig. 1. Thermoanalyzer (Mettler) and quadrupole mass spectrometer (Balzers) combined by an inlet system for simultaneous DTA–TG–MS.

at 10°C min^{-1} in a quartz oven (inside diameter 26 mm) in flowing air and argon, respectively. The gas was drawn from the oven by a peristaltic pump at a flow-rate of 1.6 l h^{-1}. About 10 mol percent of the gas stream leaving the oven was drawn by a rotary pump (0.42 l h^{-1}) through a capillary and passed, as a viscous stream, a variable leak valve (Varian 951-5100). The capillary, made from stainless steel, had an inside diameter of 0.2 mm and a length of 100 cm. During all experiments the pressure in the leak valve was 0.5 torr. According to the opening of the leak 1–2 mol percent entered the high vacuum in the MS unit. The pressure in the MS unit during all experiments was $2 \cdot 10^{-5}$ torr, produced by a turbomolecular pump (70 l sec^{-1}). The whole inlet system was heated to 150°C. The analyzer worked with 40 eV electron-energy and 10^{-10} A ion current. The selected masses (*m/e*, mass divided by charge) $2(H_2^+)$, $17(OH^+)$, $18(H_2O^+)$, $22(CO_2^{2+})$, $28(CO^+)$ and $44(CO_2^+)$ were registered continuously by a printer working synchronously with the printer from the thermoanalyzer. The peak area of the ion currents was determined by weighing.

RESULTS

The results of the thermoanalytical investigation of $CaC_2O_4 \cdot H_2O$, $NaHCO_3$ and Opalinuston are presented in Figs. 2–6. After determination of the linear regression we obtained the following equations for the straight lines in Fig. 3:

m/e 17 $y = 0.284\,x - 0.077$
18 $y = 0.067\,x - 0.001$
22 $y = 0.830\,x - 0.049$
28 $y = 0.067\,x - 0.002$
44 $y = 0.109\,x + 0.01$

For the investigation of 20 mg oxalate we determined for *m/e* = 18 according

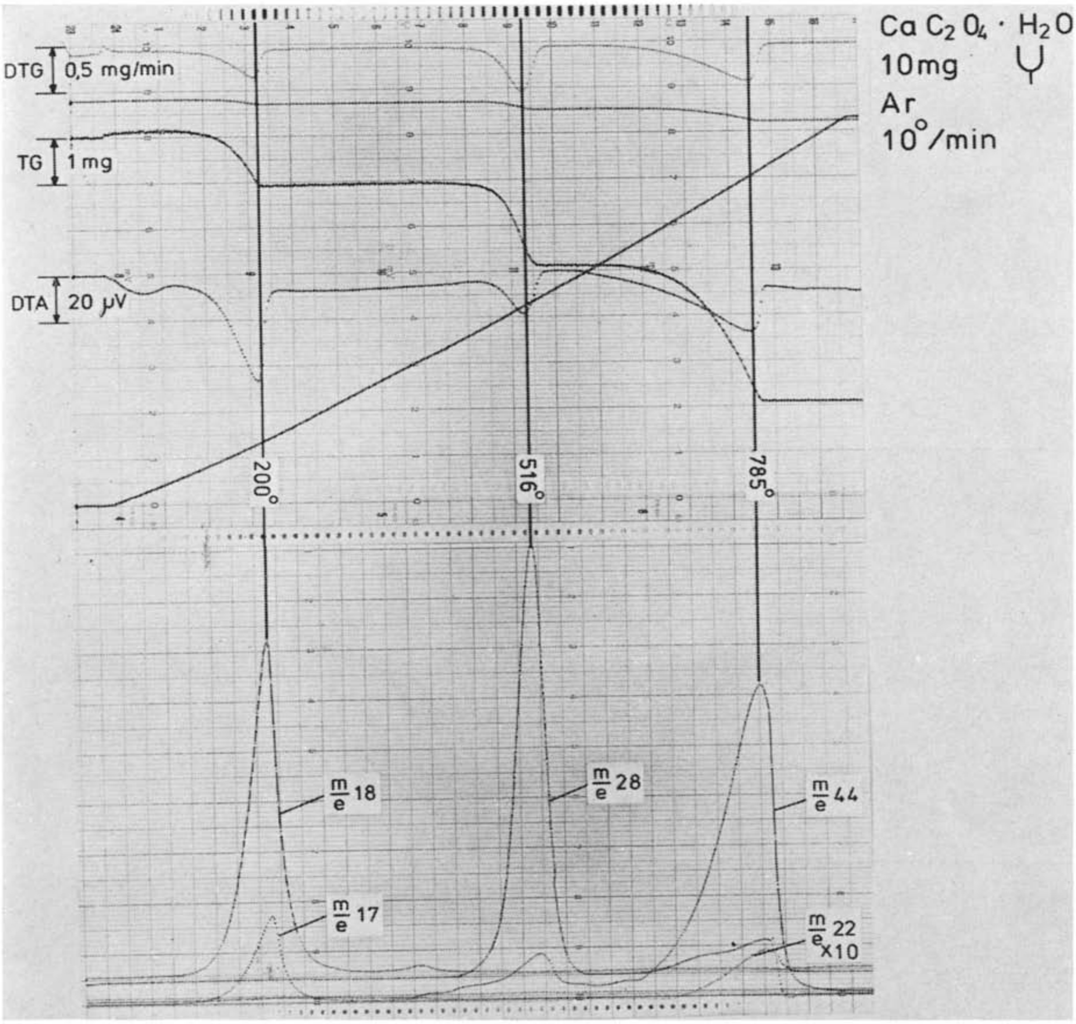


Fig. 2. DTA–TG–MS of 10 mg $CaC_2O_4 \cdot H_2O$ in argon. Heating rate 10 °C min^{-1}.

to 2.45 mg H_2O a peak area of only 30.5 As · 10^{-9} and for m/e = 44 according to 6.0 mg CO_2 only 49.5 As · 10^{-9} (see Fig. 3). Working with a heating rate of 4 °C min^{-1} we determined the values we expected, i.e., both peak area values lay on the straight lines.

DISCUSSION

The peak area of the ion current of the masses 17, 18, 22, 28 and 44 increased in air and argon linearly with the sample weight of oxalate and the straight lines crossed the x- and y-axis near the zero point (Fig. 3). Investigating 20 mg oxalate according to 2.45 mg H_2O and 6.0 mg CO_2 we determined peak areas which were too small. On the other hand we determined for the masses 17 and 22 the values we

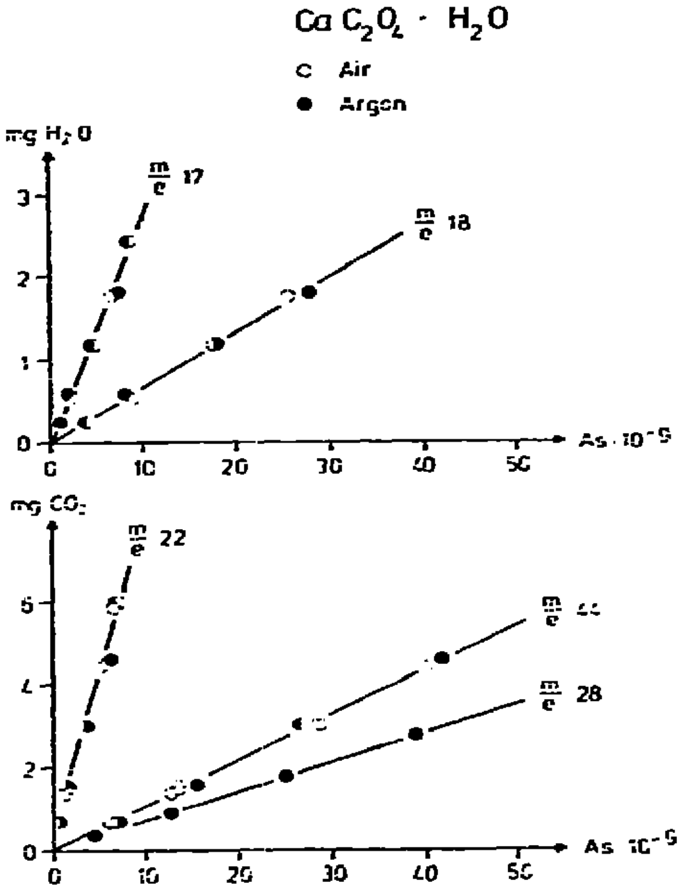
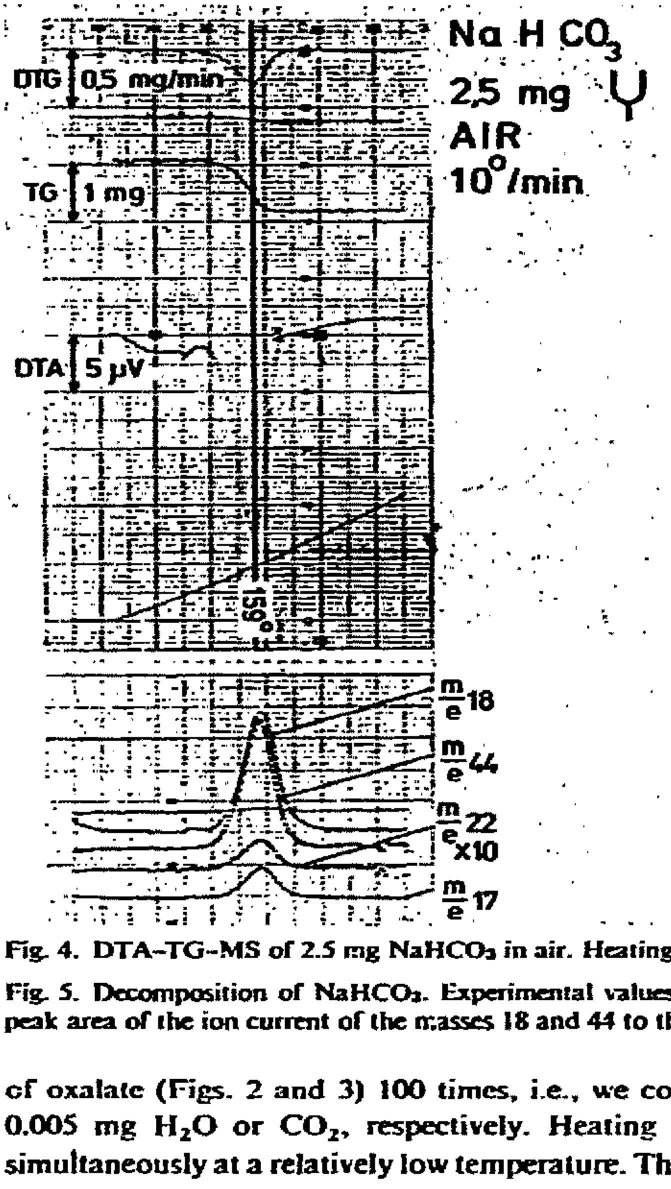


Fig. 3. Peak area of the ion current of the masses 17, 18, 22 and 44 to the weight of the evolved H_2O, CO and CO_2.

expected, i.e., values on the straight lines (Fig. 3). Heating at 6 and 4°C min^{-1}, respectively, the peak area of the masses 18 and 44 became greater, but the peak area of the masses 17 and 22 did not change. According to this the gases reached the MS unit in the correct proportion but could not be determined quantitatively by the analyzer. Under the experimental conditions used, a linearity between the peak area of the ion current of the selected masses and the weight of the evolved H_2O, CO and CO_2 could be found only up to an ion current of $0.9 \cdot 10^{-10}$ A. Exceeding this maximum ion current, it was no problem to get the correct values by repeating the investigation with a smaller sample weight or a lower heating rate, respectively. On the other hand we did not change the calibration conditions, i.e., the flow-rate of the carrier gas, the pressure above the leak and in the MS unit and the adjustments of the analyzer. The most delicate part of the inlet system is the capillary. Even the smallest clogging of the capillary is immediately detectable by alterations in the pressure above the leak and the MS unit. Some gases such as O_2, HCl and SO_3 are retained by the capillary. We could have magnified the ion current measured in the investigation



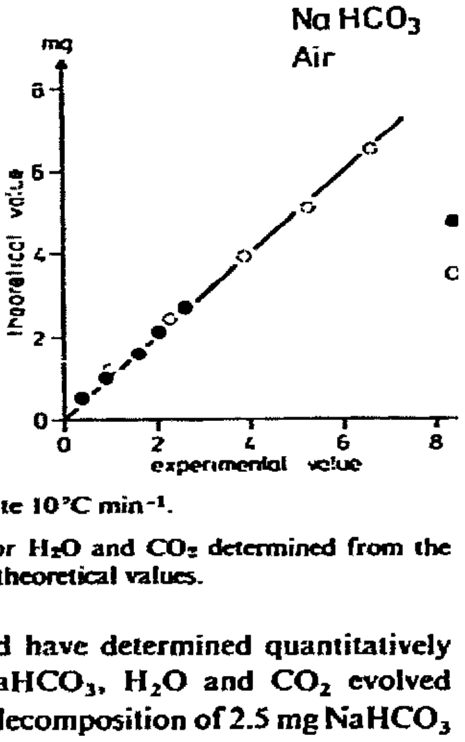


Fig. 4. DTA-TG-MS of 2.5 mg $NaHCO_3$ in air. Heating rate 10°C min^{-1}.

Fig. 5. Decomposition of $NaHCO_3$. Experimental values for H_2O and CO_2 determined from the peak area of the ion current of the masses 18 and 44 to the theoretical values.

of oxalate (Figs. 2 and 3) 100 times, i.e., we could have determined quantitatively 0.005 mg H_2O or CO_2, respectively. Heating $NaHCO_3$, H_2O and CO_2 evolved simultaneously at a relatively low temperature. The decomposition of 2.5 mg $NaHCO_3$ (Fig. 4) reveals both gases to be determined by the MS nearly without retardation, whereby the ion current would have been increased by a factor of 10. As Fig. 5 shows, we could determine the theoretical values of the weight loss from the peak area of the ion current. Figure 6 shows a thermoanalytic mass spectrometrical investigation of Opalinuston (2–0.2 µ) in air and in argon, respectively. The sample contained different clay minerals, carbonates and organic matter. The organic matter decomposed at 335 and 480°C, indicated by the exothermic reactions and the evolved H_2O and CO_2. These reactions could not be observed when the investigation was carried out in an argon atmosphere. The second step in the decomposition of the organic matter overlapped with the dehydroxylation of the clay minerals (540°C) and the Siderite decomposition (512°C), the latter also clearly indicated by DTG.

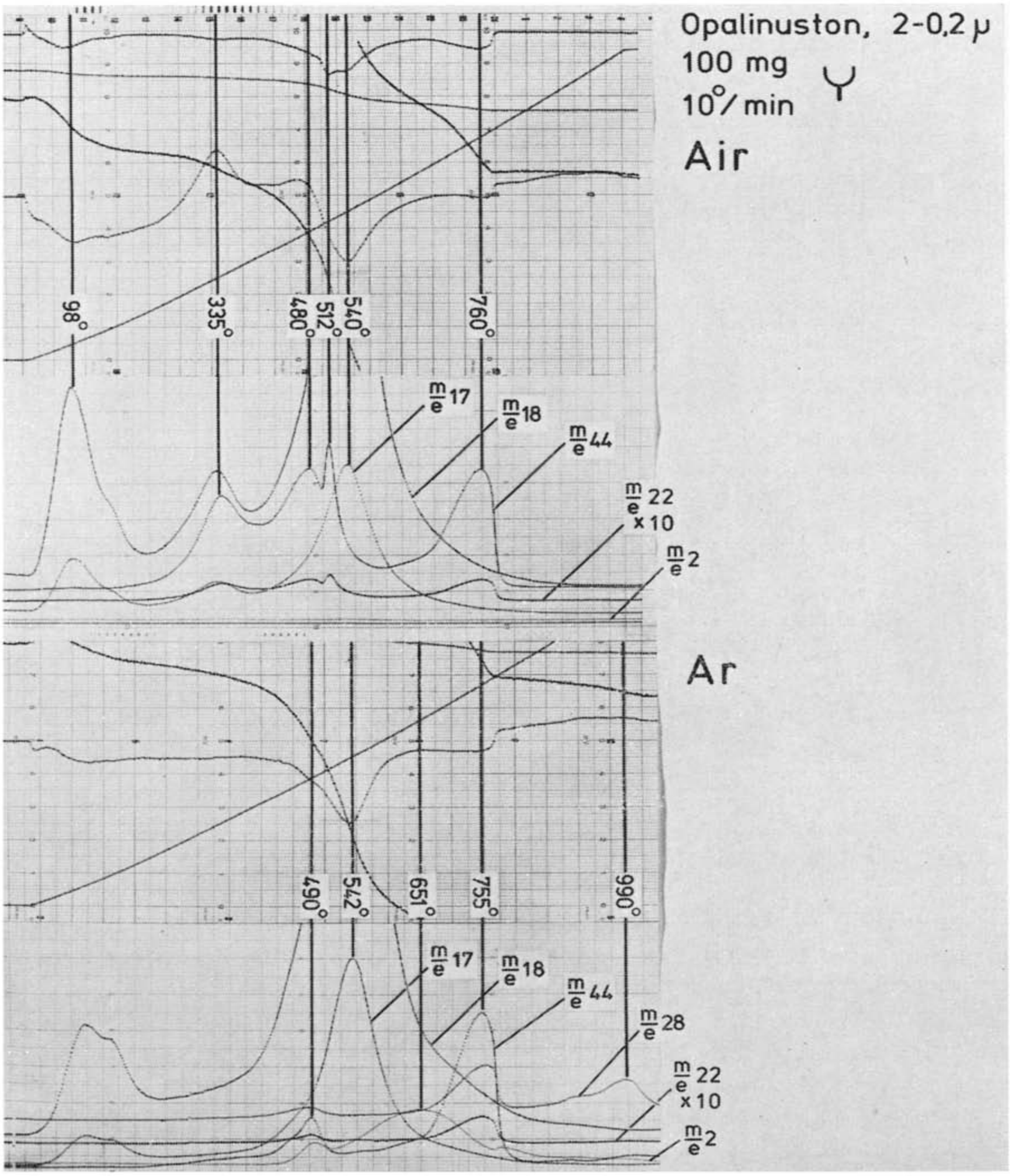


Fig. 6. DTA-TG-MS of 100 mg Opalinuston, 2-0.2 µ in air. Heating rate 10°C min^{-1}.

At about 600°C the decomposition of Calcite started. By evolved gas analysis with MS we determined:

	Organic matter		*Siderite*	*Dehydroxylation*	*Calcite*
	335°C mg CO_2	*480°C mg CO_2*	*(mg)*	*(mg H_2O)*	*(mg)*
air	2.37	2.17	2.21	6.55	6.75
argon			2.20	6.41	6.77

At the first step in the decomposition of the organic material (335°C) we also determined 1.34 mg water. However, at the second step in the decomposition we could not detect a release of water. We believe these two steps at 335 and 480°C, respectively, must indicate two different fractions of the organic matter. Up to now, our experiments have indicated that our DTA–TG–MS equipment may be useful in revealing the rank of coalification.

REFERENCES

1 J. W. Smith in H. G. Wiedemann (Ed.), *Thermal Analysis, Proc. 3rd ICTA*, Vol. 3, 1971, p. 605.

2 M. Müller-Vonmoos and R. Müller, in I. Buzás (Ed.), *Thermal Analysis, Proc. 4th ICTA*, Vol. 2, 1974, p. 521.