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Simultaneous thermogravimetry–differential thermal analysis–mass spectrometry (TG–DTA–MS) using a heated capillary interface [1]

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Abstract

A quadrupole mass spectrometer (MS) has been successfully and simply coupled to a simultaneous thermogravimetric analyzer–differential thermal analyzer (TG–DTA) through a heated capillary interface. The system has been used to study both calcium oxalate monohydrate and to interpret the unusual vaporization behavior of Buckminsterfullerene C_{60} on heating in an inert atmosphere.

INTRODUCTION

Hans Wiedemann has been a pioneer in analytical thermal analysis who, in addition to developing individual instruments such as the thermogravimetric analyzer (TG) [1], was also a believer in the usefulness of combined techniques, as was most recently evidenced by the commercialization of his simultaneous DSC–thermal microscopy technique [2]. The simultaneous use of two techniques has proliferated over the last twenty-five years with the introduction of TG–DTA, TG–MS, TG–FTIR, DTMA–DETA and other evolved gas analyzer combinations by the instrument manufacturers. There are, in contrast, fewer examples of combinations of three techniques and those that exist usually combine TG–DTA with either FTIR or MS. This paper exemplifies the latter combination by using a simple coupling mechanism between commercially available TG–DTA and MS instruments.

"If one technique is good, two are better, and three are better still" when it comes to characterizing materials. Using this as a working hypothesis, we have coupled a mass spectrometer to a simultaneous TG–DTA via a

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[1] Dedicated to Hans Georg Wiedemann.

heated capillary interface, in the belief that it is better to examine one sample under identical ambient and heating conditions using all techniques than to optimize separate samples for each technique. In this way, subtle effects can be observed more easily than in individual techniques in which experimental variables such as sample size and shape, ambient atmosphere and flow rate, temperature calibration and control, together with heat and mass transfer effects, may obscure the differences.

EXPERIMENTAL

A 320 TG–DTA (Seiko Instruments) was coupled to a VG Micromass 300D mass spectrometer (Fisons Instruments) through a standard heated capillary interface (Fisons) in a manner previously used for TG–MS [3]. Direct coupling to the ceramic furnace tube (FTIR-type) of the TG was made using a simple machinable-ceramic (Macor) insert as shown in Fig. 1. This insert allowed the co-axially-centered, four-holed alumina tube, containing the capillary inlet and heating wire, to approach the sample pan to within 2–5 cm without heating it. Outwith the TG–DTA furnace, the 0.3 mm i.d. ×1.8 m long fused silica capillary was heated by applying a low a.c. voltage across the ends of a close-fitting, stainless steel sheath surrounding the capillary that was, in turn, thermally insulated. A variable transformer was used to apply 30 V which gave a transfer line temperature in the range 180–200°C.

The mass spectrometer was first used to determine the time necessary to purge the TG–DTA when the ambient gas was changed by switching gas cylinders. Figure 2 shows the sequence air–argon–air as a function of gas flow rate (a) 500 ml min^{-1}, (b) high flow rate (off scale on flowmeter, about 1000 ml min^{-1}). At 500 ml min^{-1}, a purge of 25–30 min was necessary to reach background levels of N_2 and O_2 but an increase in flow rate reduced this time to 15 min. Replacement of argon by air, however, took slightly longer taking 35 and 25 min, respectively, for the two flow rates. In addition, it was observed that air could circulate back into the balance

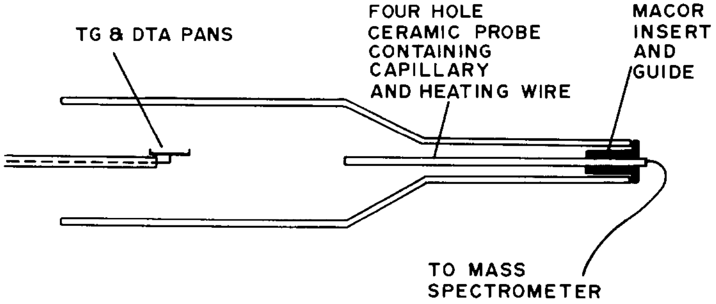

Fig. 1. Schematic diagram of the simple ceramic (Macor) coupling between MS and TG–DTA.

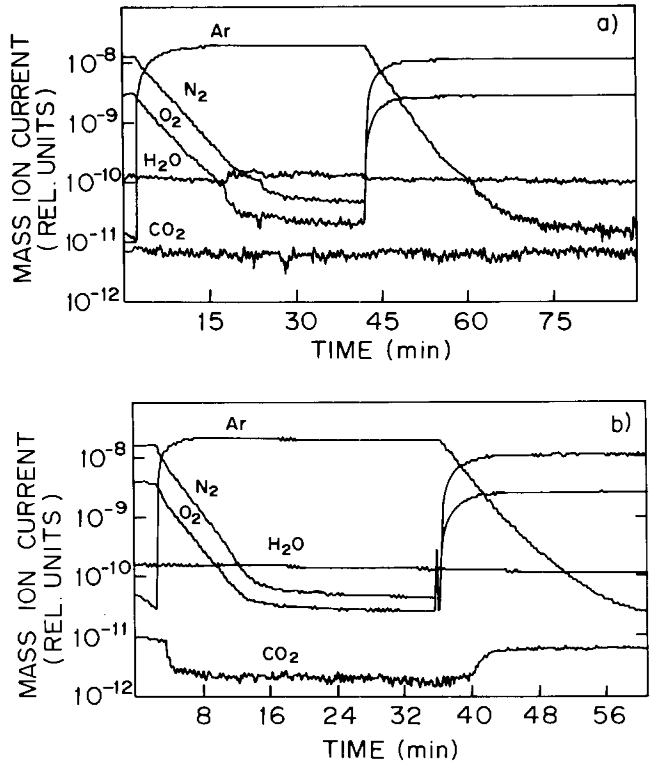

Fig. 2. Time dependence of gas exchange rates in a Seiko 320 TG–DTA for air–argon–air as a function of flow rate: (a) 500 ml min^{-1}; (b) >1000 ml min^{-1}.

housing while the sample was being loaded at normal purge flow rates of 100–300 ml min^{-1}. Hence, it is recommended that the ambient gas flow be increased to high flow rate during loading and be maintained for 5–10 min on closing, if the presence of traces of O_2 could affect the behavior of the sample on heating. An example of this phenomenon is given below. In Fig. 2(b) it can be observed that the higher argon flow rate causes a significant decrease in the background level of CO_2 which is not observed at the lower flow rate. The reason for this is not obvious but may be due to suppression of back diffusion of air through the four-holed alumina tube.

Another normal precaution that should be taken when using this simultaneous technique is to remove any condensate that may have accumulated on the ceramic furnace tube from a previous run. This can be accomplished either by programmed heating to a high temperature in air or by removing and heating the tube in air to burn off the condensate. Either of these procedures should prevent spurious MS signals from appearing during a run.

Mass spectra can be taken and stored in a variety of modes with this spectrometer: as linear or logarithmic analog scans, linear or logarithmic histogram scans and in a Multiple Ion Monitoring mode in which up to sixteen selected masses can be continuously monitored. In these experiments, MS data were accumulated in the "log histogram" mode. A complete mass spectrum was taken over a predetermined mass range approximately every 20 s (depending on the mass range) and stored as a function of time. The time evolution of a specific mass number could then be extracted from the data set and plotted on a logarithmic scale, as shown in Fig. 2, thus allowing both the most abundant and least abundant gases to be plotted simultaneously. When only one logarithmic decade is selected for the ordinate, the intensity of the mass ion current is plotted on a linear scale.

APPLICATIONS

Decomposition of calcium oxalate monohydrate

As a check on the efficiency of this system, the standard calibration material used in thermogravimetric analyzers, calcium oxalate monohydrate, was examined. A 9.88 mg sample of $CaC_2O_4 \cdot H_2O$ (standard calibration sample supplied by Seiko Instruments) was heated from room temperature to 900°C at 20°C min^{-1} on the TG–DTA–MS system under 100 ml min^{-1} argon flow and mass spectral data collected in the "log histogram" mode in the range 12–50 Daltons. Figure 3(a) shows the combined TG, DTA and DTG data as a function of temperature compared with the MS data (Fig. 3(b)) which was collected only on time base and transformed into a temporal display of the intensity of the specific masses shown (18 is H_2O, 28 is N_2 or CO, 32 is O_2 and 44 is CO_2). A logarithmic plot allows three decades of intensity to be observed but the shape of the peaks can only be directly compared with the DTG curve when both are plotted on a linear scale (see Fig. 4). Evolution of water, CO (note that this baseline is due to residual N_2 in the mass spectrometer) and CO_2 can be clearly observed, corresponding to the three mass loss regimes in the decomposition scheme shown in Table 1. Excellent agreement between theory and experiment was obtained for mass loss. In addition, it can be observed in Fig. 3 that a close correspondence exists in the positions of the maxima in DTA, DTG and MS. If we compare the maximum rate of mass loss in each step with the maximum ion current observed above the baseline value at each step (adding both the CO and CO_2 signals), then a very close correspondence is obtained (step 1, 5.2 wt.% min^{-1}, $\approx 5 \times 10^{-11}$ (mass ion current); step 2, 7.4 wt.% min^{-1}, $\approx 7.3 \times 10^{-11}$; step 3, 7.6 wt.% min^{-1}, $\approx 7 \times 10^{-11}$) indicating that the assumption of a constant ionization efficiency (of about unity) is reasonable for H_2O, CO and CO_2. When we compare these results with the ion current of the ambient gas (1.2×10^{-8})

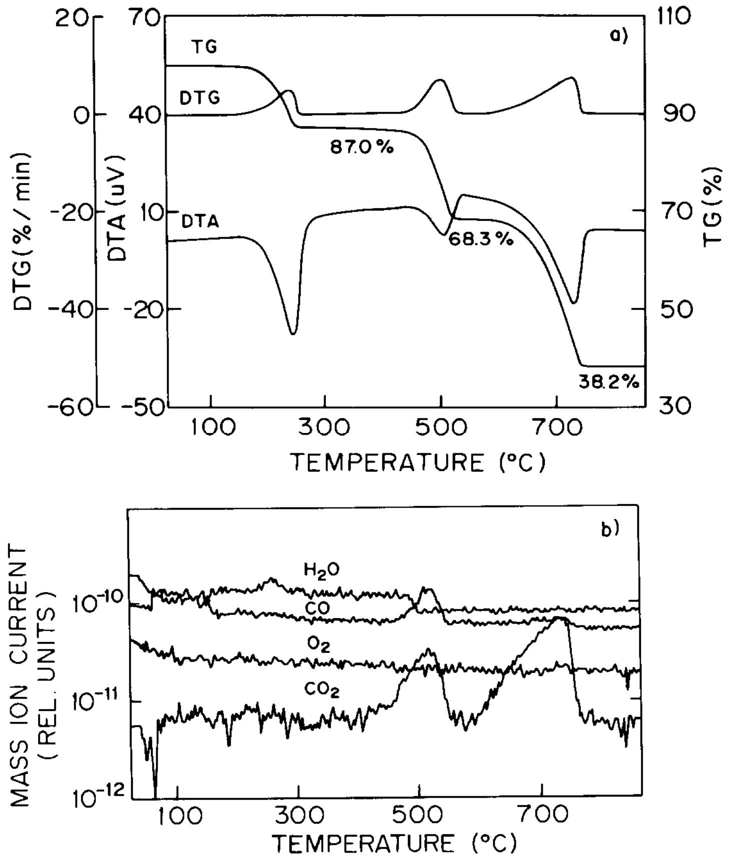

Fig. 3. TG–DTA–MS scan for the decomposition of calcium carbonate monohydrate, $CaC_2O_4 \cdot H_2O$, under argon: (a) combined TG, DTA and DTG scans; (b) logarithmic display of MS data.

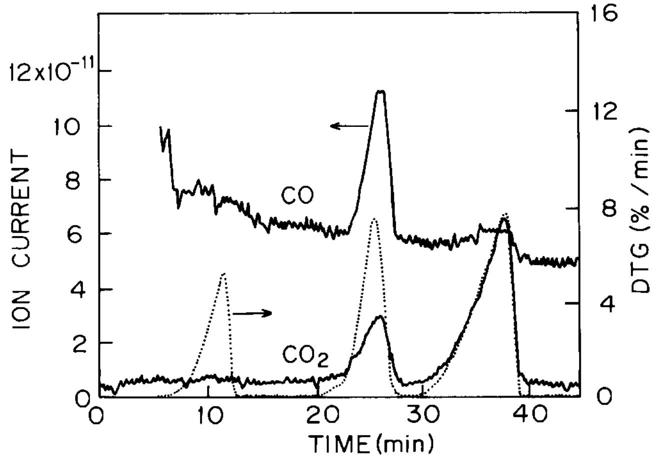

Fig. 4. Comparison of DTG curve with MS data on a linear scale for $CaC_2O_4 \cdot H_2O$ decomposition.

TABLE 1

Decomposition of calcium oxalate monohydrate $CaC_2O_4 \cdot H_2O$

Step	Reaction	Total mass loss/%	
		Theory	Expt.
1	$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O\uparrow$	12.3	13.0
2	$CaC_2O_4 \rightarrow CaCO_3 + CO\uparrow$	31.5	31.7
3	$CaCO_3 \rightarrow CaO + CO_2\uparrow$	61.7	61.8

which is argon flowing at 100 ml min^{-1} (about 180 mg min^{-1}), we find that an ion current of 5×10^{-11} corresponds to $(5 \times 10^{-11}/1.2 \times 10^{-8}) \times$ 180 mg min^{-1} = 7.2 mg min^{-1} which compares favorably with the actual rate of decomposition of $0.052 \times 9.88 = 5.1$ mg min^{-1}, in the case of step 1. Hence a semi-quantitative agreement exists for these gases and an approximate correlation can be made between mass loss and gas evolved. This gives one confidence in confirming that the mass loss measured is totally due to the mass observed. For systems in which the ionization efficiency of the evolving gas or vapor is not known, this agreement clearly cannot hold. Note also that, in this case, partial oxidation of the CO evolved occurs as does partial reduction of the CO_2.

The detection sensitivity of this instrument depends on the background level of the ion being measured. If the mass ion has zero background then, in principle, a 100 mg sample evolving a gaseous product with an ionization efficiency of unity could be detected at the 1–10 ppm min^{-1} level in an ambient gas flow of 100 ml min^{-1}.

C_{60}, Buckminsterfullerene

An example of a material in which the use of combined TG–DTA–MS equipment has proved invaluable is that of buckminsterfullerene, C_{60}. Over the last few years extensive studies have been made on the fullerenes, a new class of pure carbon compounds of which C_{60} is the most stable and abundant member [4, 5].

TG–DTA–MS has been used to evaluate the purity of this material with respect to occluded solvent and to elucidate unexpected phenomena observed during vaporization at high temperature [6]. Figure 5 shows combined TG–DTA and MS data observed at high temperature for two samples of C_{60} which differ only in the background level of oxygen. In Fig. 5(a) a large endotherm is observed as C_{60} sublimes (DTA indicates that no melting occurs below 1000°C) and the MS shows a small increase in the background level of CO_2 at high temperature whereas in Fig. 5(b) almost no endothermic process can be observed as C_{60} sublimes and the MS shows

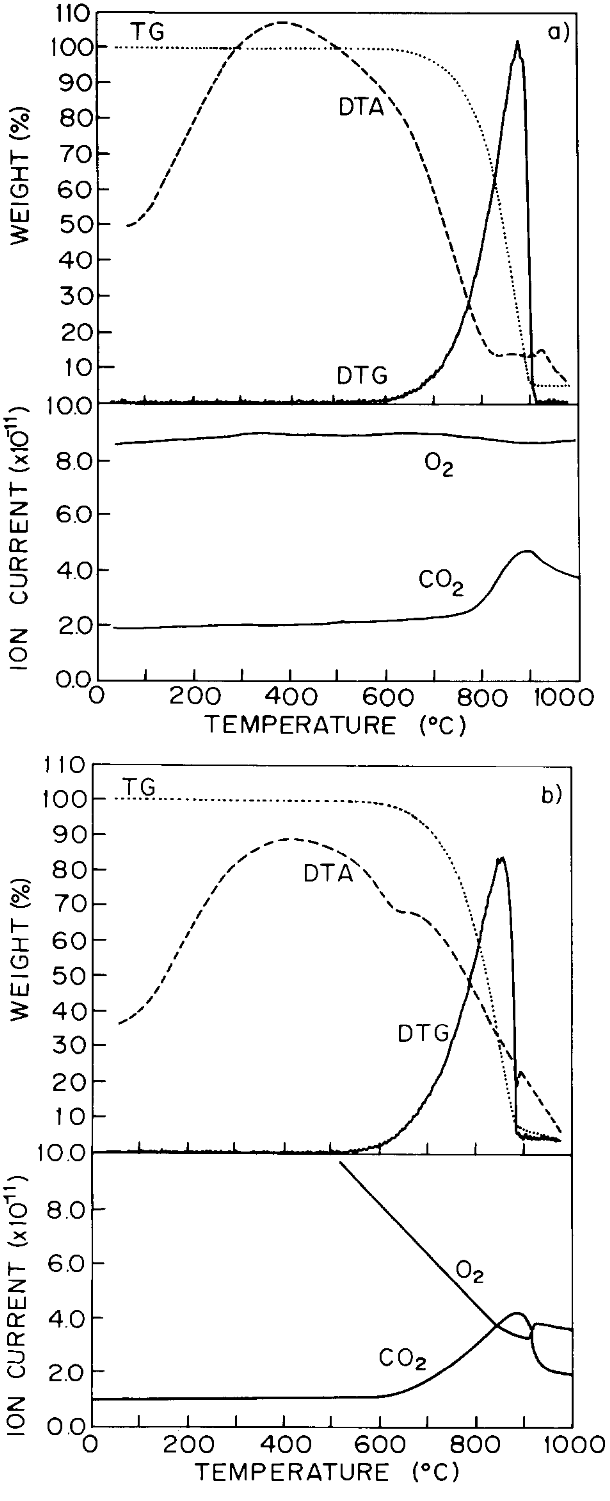

Fig. 5. Combined TG–DTA–MS scans for C_{60} under argon for, (a) sample run under a low, steady state oxygen background level; (b) sample run under a non-steady state oxygen level.

both an increased level of CO_2 evolution coupled with oxygen absorption from the background oxygen level in the ambient gas. In the latter case, exothermic production of CO_2 appears to compensate the endothermic heat of sublimation observed in Fig. 5(a).

In addition, the TG–DTA data in Fig. 5(a) show that the DTG curve does not correspond with the observed endothermic process. There is a large displacement in the maximum position of each which varies with the oxygen level in the ambient gas. It should also be noted that the signal sensitivity in Fig. 5(b) was twice that in Fig. 5(a); hence the effect is actually more pronounced than it appears in the figure.

Attempts to quantify the endothermic heat of sublimation of C_{60} from the DTA curves were made by calibrating the system using the heats of melting of In (m.p. 156.6°C), Zn (m.p. 419.6°C) and Ag (m.p. 962°C) as reference materials. A calibration curve similar to that observed by Gallagher and Zhong [7] for the same type of instrument was obtained. However, large heats of sublimation were calculated (about 600–800 kJ mol^{-1}) which are not consistent with values obtained by effusion measurements (about 170 kJ mol^{-1} [8]) although an activation energy of 162 kJ mol^{-1} was observed for the sublimation process by TG in this experiment. The reason for this discrepancy has not been fully determined at present and will be the subject of a future publication.

CONCLUSION

We have demonstrated a simple method of coupling a quadrupole mass spectrometer to TG–DTA and shown its usefulness for semiquantitative analysis of gases and vapors evolved from calcium oxalate monohydrate. We have also applied this technique to resolve a dilemma in the interpretation of TG–DTA data on buckminsterfullerene. A case clearly exists for widespread application of simultaneous TG–DTA–MS and precise information can be obtained simply and rapidly by this technique which cannot be obtained in any other way.

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