

Evolved gas analysis of inorganic compounds with a quadrupole mass spectrometer coupled to a thermogravimetric analyzer

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Abstract

An inexpensive EGA system, based on a quadrupole MS and a standard PC, has been constructed and connected to a commercial thermobalance *via* a heated capillary. The system has been tested with various inorganic compounds including $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Pt}(\text{NH}_3)_5\text{OH}]\text{Cl}_3 \cdot \text{H}_2\text{O}$. The applicability of the TG-EGA-MS system is discussed.

1. INTRODUCTION

Combining thermal analysis (TA) with gas-analytical techniques significantly enhances the possibilities for correctly interpreting the mechanisms of thermally induced reactions which involve gaseous species. Several techniques can be used for evolved gas analysis (EGA) ranging from simple detection methods (EGD) to the more elaborate ones involving gas chromatography (GC), IR or MS spectroscopy for gas detection and analysis [1]

While the GC methods were used already in the 1960s [2], EGA by FTIR was described much later and used for the analysis of pyrolytic and combustion products [3,4]. Presently, there are several commercially available FTIR systems which can be coupled to a thermogravimetric (TG) analyzer, for instance [5,6].

Mass spectrometry offers several advantages for evolved gas analysis including besides high sensitivity, the possibility for a simultaneous, unequivocal and fast detection of several gaseous species within the available mass range. The first EGA-

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MS systems were reported some 20 years ago, but they involved differential thermal analysis (DTA) [7] or pyrolysis [8] rather than TG because the latter needs a more elaborate inlet system to transport the evolving species into the MS. The first report of a TG-MS combination dates from 1968 and it employed a time-of-flight spectrometer [9]. The first system based on a quadrupole MS was described somewhat later [10] and it was successfully used for the study of lunar soil samples [11]. The early developments of EGA-MS have been reviewed by Friedman [12] and Langer [13].

When a TA instrument - in particular a TG analyzer - is coupled to a mass spectrometer, the essential problem is how to construct the interface. Two basically different approaches can be used: (i) coupling directly under vacuum or (ii) letting the thermobalance to work under atmospheric pressure and reducing the pressure through interface. The first type restricts the TG experiments to those under high vacuum as the operating pressures of mass spectrometers typically are 10^{-8} ... 10^{-10} atm. Only the chemical ionization type mass spectrometers tolerate intermediate pressures ($>10^{-3}$ atm) [14,15].

Several interface constructions have been reported for an atmospheric pressure TG-MS coupling, including the capillary [16-18], double orifice [19] and jet separator systems [20]. The various approaches and their applications have been reviewed by Dollimore *et al.* [21], Holdiness [22] and most recently by Szekely *et al.* [23].

It is generally recognized that EGA-MS significantly enhances the possibilities of TG because the gaseous species with nearly the same masses (e.g. H_2O and NH_3) can be identified and overlapping reactions resolved. Nevertheless, its wider application has been hampered by the high cost of commercially available instruments.

2. EXPERIMENTAL

2.1. Aim of the work

The purpose of the present work was to construct an inexpensive PC-controlled EGA-MS system which could be coupled to an existing TG instrument (Perkin-Elmer TGA 7) and used to monitor the reactions of inorganic compounds and complexes. A further goal was to make the system portable so that it could be moved to study the atmosphere in a reactor used for thin film depositions [24].

2.2. Coupling of mass spectrometer to the thermobalance

In order to limit the costs and constructional changes in the thermobalance to a minimum, the pressure difference between the TG analyzer and the mass spectrometer was compensated *via* a heated capillary interface. The sampling was done by a quartz

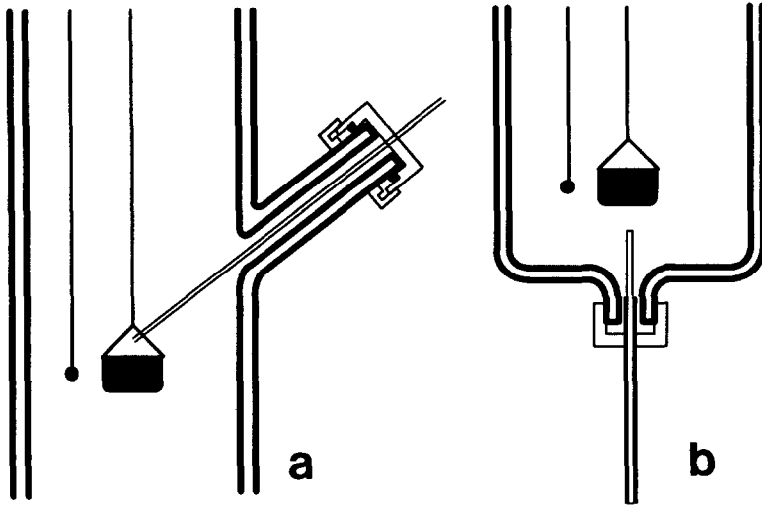


Figure 1. Gas sampling in the case of normal (a) and high-temperature (b) furnace.

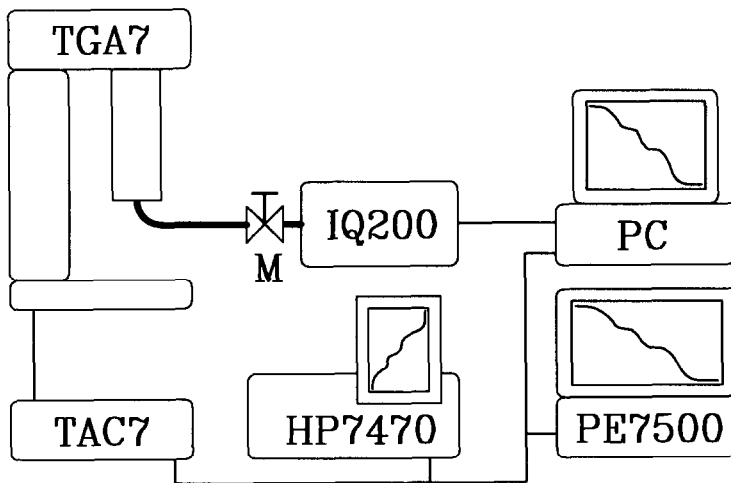


Figure 2. Configuration of the TG-EGA-MS system.

tube which had its tip about 1 mm above the sample pan in the quartz oven (Fig. 1a). A short distance is essential in order to get a large enough representative sample [25]. When the high temperature oven was used the sampling was carried out from underneath which led to a dilution of the evolved gases with the helium purge gas (Fig. 1b).

Figure 2 shows a block diagram of the TG-MS system for evolved gas analysis. The thermogravimetric analyzer TGA 7 is controlled by the Perkin-Elmer PE 7500 computer via the TAC 7 instrument controller. The data exchanged by the PE 7500 and TAC 7 is monitored by a general-purpose personal computer (PC). The PC also controls the Leybold-Heraeus IQ 200 quadrupole mass spectrometer (mass range 200 amu), which can scan up to 10 preselected m/z values. Both computers can send their output to the HP 7470 plotter. Gas exiting the TGA 7 is directed to the mass spectrometer through a pressure reducing capillary tube and a molecular-leak valve. The 0.5 m long and 0.32 mm inner diameter deactivated fused silica capillary (HNU-Nordion, Helsinki) is enclosed within a 0.5 mm inner diameter steel capillary which is heated to approximately 150 °C during the measurements.

The Perkin-Elmer computer is also used to perform the TG runs. The attached PC does not have the capability to control the TG but it can monitor and record sample temperature and weight during a TG analysis. Additionally, it can record the composition of evolved gases as obtained from the IQ 200 mass spectrometer. The EGA results can be overlaid with the output produced by the TG system enabling quick analysis of the thermal decomposition process.

3. RESULTS AND DISCUSSION

3.1. Performance of the system

The compounds used to check the overall performance of the system included the standard test substances, viz. $\text{CuC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ which decompose in several steps below 1000 °C and evolve neutral (H_2O , CO), basic (NH_3) as well as acidic (CO_2 , sulfur oxides) gases. All test runs were carried out using the high temperature oven and helium as carrier gas. The heating rate was 10 °/min.

Fig. 3 depicts the TG and EGA-MS curves for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ which were obtained for clarity with a relatively large sample size. The three reaction steps (1) $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}(\text{g})$, (2) $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}(\text{g})$ and (3) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2(\text{g})$ are well resolved. Because of the disproportionation equilibrium $2 \text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$, the steps 2 and 3 involve both CO and CO_2 [26]. The ratio of the carbon oxides depends on the heating rate and catalytic effects [26,27]. Residual oxygen will

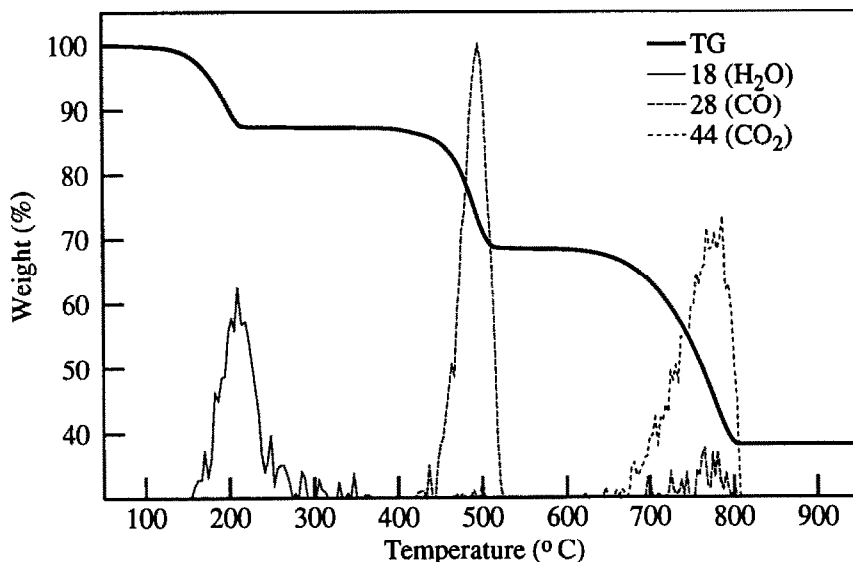


Figure 3. TG and EGA-MS curves of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Sample weight 92.6 mg.

also lead to an increase of CO_2 during step 2 and therefore prolonged pumping is important before the runs as was done for Fig. 3.

The TG-EGA curves for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were recorded using a relatively high heating rate in combination with a large sample size. Therefore the trihydrate intermediate is not seen in the curves but the dehydration proceeds directly to the monohydrate (Fig. 4). Above 700 °C the anhydrous sulfate begins to decompose and the reactions $\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_3$ and $\text{SO}_3 \rightleftharpoons \text{SO}_2 + 1/2 \text{O}_2$ explain the peaks at m/z 64 (SO_2) and 32 (O_2) [28]. The final weight loss at 850–900 °C is due to the reaction $2 \text{CuO} \rightarrow \text{Cu}_2\text{O} + 1/2 \text{O}_2$.

In the case of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$, the EGA-MS data are essential to resolve the overlapping reactions (Fig. 5). In agreement with the earlier EGA-MS studies [28,14] water and ammonia are released first, the latter in three distinct steps corresponding to 2, 1 and 1 moles, respectively. While the main part of water is expelled by 250 °C there appear to be small bursts of water associated with the second and third ammonia release, too. Langer and Brady have observed similar behaviour for the same compound in their EGA experiments in an argon atmosphere [29]. The two last weight losses at 700–850 °C and 900–950 °C are due to the decomposition of CuSO_4 and CuO , respectively, but instead of SO_2 another sulfur oxide SO was detected by mass spectrometry.

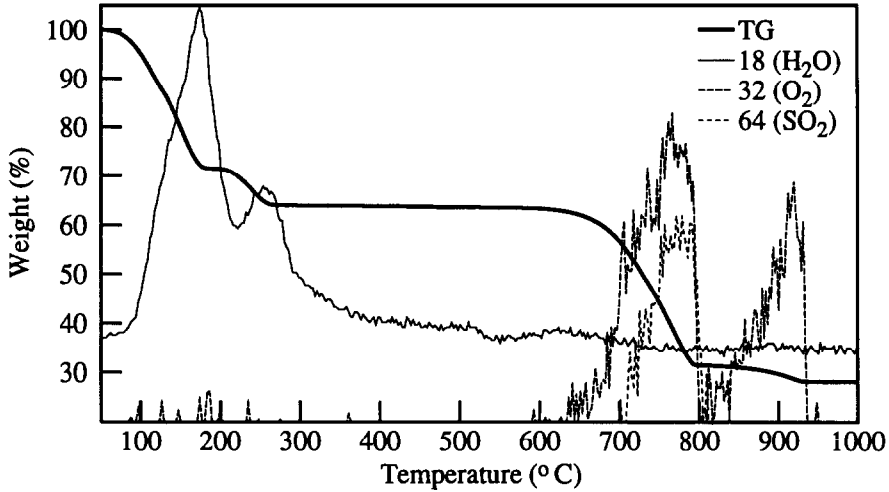


Figure 4. TG and EGA-MS curves of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Sample weight 55.9 mg.

Originally, sulfur trioxide is released but because its decomposition $\text{SO}_3 \rightleftharpoons \text{SO}_2 + 1/2 \text{O}_2$ is endothermic and the reaction products are swept away, SO_3 cannot exist at higher temperatures. SO_2 may also decompose: $\text{SO}_2 \rightarrow \text{SO} + \text{O}$; this reaction is promoted by high temperature and low pressure [30]. Nevertheless, it was unexpected to find SO only for $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ and not for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ where the experimental conditions were quite similar. Collins *et al.* [28] have also reported the presence of SO when CuSO_4 and other metal sulfates were heated and attributed this to SO_2 decomposition in the ionization chamber of the mass spectrometer [11]. This is a plausible explanation here, too

Test runs described above indicated that the system works in a satisfactory manner and detects inorganic gases evolving from a solid sample. The heated capillary interface is especially suitable for gases such as O_2 , N_2 , CO, CO_2 and NH_3 while water tends to be retained in the column causing the peaks to be relative broad and to have tails. For the best results, the silica capillary should be changed often and the vacuum pumping prior to the experiments should be sufficiently long in order to reduce the background to a minimum; this can easily be monitored by the MS.

In practice, the most serious problems are sensitivity, especially when working with the high-temperature configuration (Fig. 1b), and clogging of the column. The former can be improved by working with relatively large samples (30–100 mg) and minimizing the "dead volume" in sampling [34]. A simple jet separator interface [20] would, in

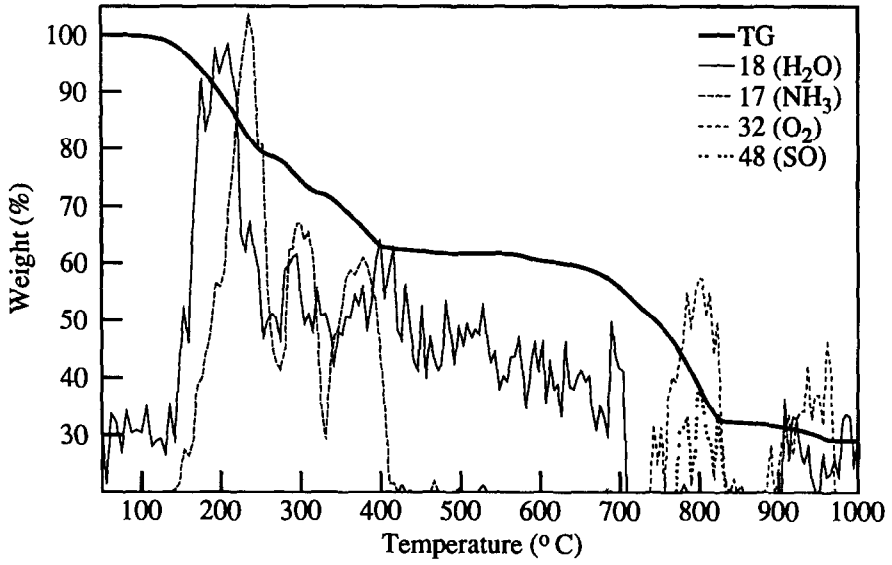


Figure 5. TG and EGA-MS curves of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$. Sample weight 133.2 mg.

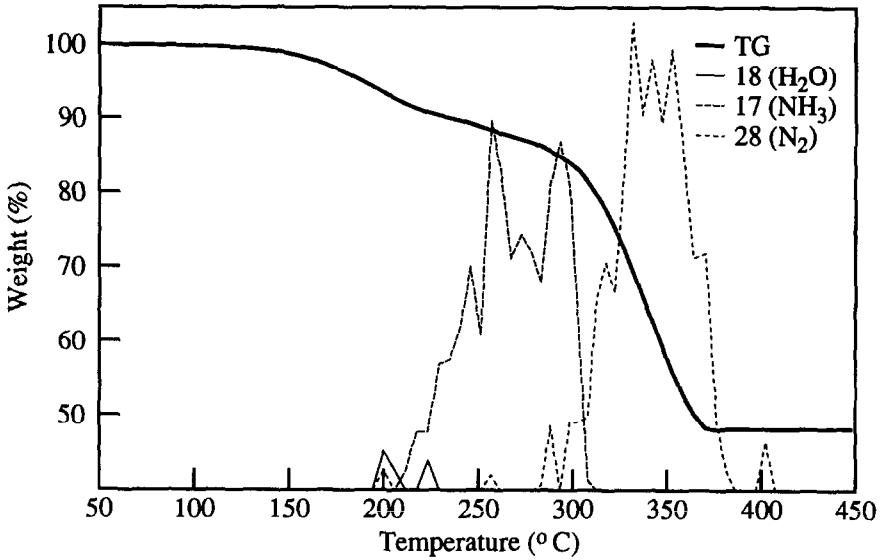


Figure 6. TG and EGA-MS curves of $[\text{Pt}(\text{NH}_3)_5\text{OH}]\text{Cl}_3 \cdot \text{H}_2\text{O}$. Sample weight 109.2 mg.

principle, be an ideal solution for these problems but in this work its geometry and operation were found difficult to optimize [25].

3.2. Applications

The EGA-MS system was applied to resolve the decomposition mechanism of a penta-ammine complex of platinum(IV), $[\text{Pt}(\text{NH}_3)_5\text{OH}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (Chugaev-Chlopin salt). The mass spectra (Fig. 6) clearly show that the last decomposition step involves the release of nitrogen thus corroborating the suggested reaction mechanism [31]. This result is another example of the usefulness of EGA-MS in the study of thermal behaviour of noble metal complexes [32,33]

Two other applications of the present system have been reported elsewhere [35,36]. During the decomposition of $\text{LaC}_2\text{O}_4\text{Cl}$ in helium, H_2O , O_2 , CO and CO_2 were detected [34]. Oxygen was also detected in a study on the carbon-free preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor using metal iodates as precursors. When $\text{Cu}(\text{IO}_3)_2$ is heated above 400 °C it decomposes with the evolution of oxygen [36].

4. CONCLUSIONS

An inexpensive EGA-MS system, based on a quadrupole MS and a PC, has been constructed and connected *via* a heated capillary to an existing thermobalance. The system can be successfully employed for analyzing evolved gases up to 200 amu as shown by several examples.

Problems encountered in the analyses include the relatively large sample size, retention (tailing) of water in the capillary column and its contamination. However, with a clean column and adequate pumping prior to the runs well resolved MS spectra can be obtained. The EGA-MS data provide valuable additional information which in most cases is essential for the correct interpretation of the TG/DTG curves [37].

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