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APPLICATIONS OF A NEW QUADRUPOLE MASS SPECTROMETER SYSTEM FOR SIMULTANEOUS THERMAL ANALYSIS - EVOLVED GAS ANALYSIS

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A recently-developed quadrupole mass spectrometer system, specifically designed for thermal analysis studies, has been linked to a thermobalance and a simultaneous TG-DTA unit, for evolved gas analysis. The performance and applicability of the system is illustrated by examples from four fields of study.

Keywords: EGA, TG-DTA-MS,

Introduction

The major thermal analysis techniques provide physical information, and ancillary data are required for chemical interpretation of the observed thermal events. Evolved gas analysis (EGA) provides a direct route to chemical information, and is most effectively performed by mass spectrometry. Additional advantages of the technique include its specificity and sensitivity. This paper describes some applications of a recently-developed quadrupole mass spectrometer system – the Thermolab (VG Gas Analysis) – specifically designed for thermal analysis studies.

Description of equipment

A schematic diagram of a Thermolab installation is shown in Fig. 1. The main unit, comprising the mass spectrometer itself (the ion source, quadrupole analyser and detector), as well as the interface, the turbomolecular pump and associated

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electronics, is compact enough to be sited on a bench top (Fig. 2). Outside this unit are a rotary pump, the computer controller, and a capillary for connection to the thermal analysis unit.

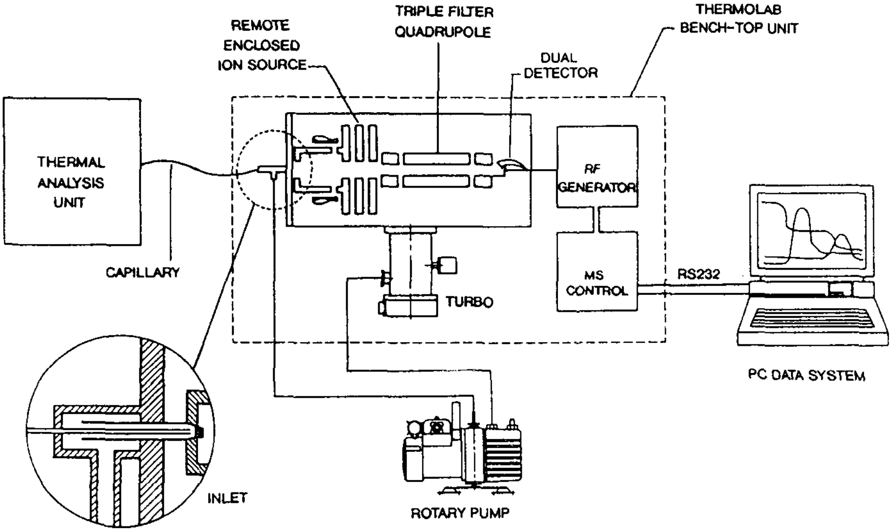

Fig. 1 Schematic diagram of a Thermolab installation

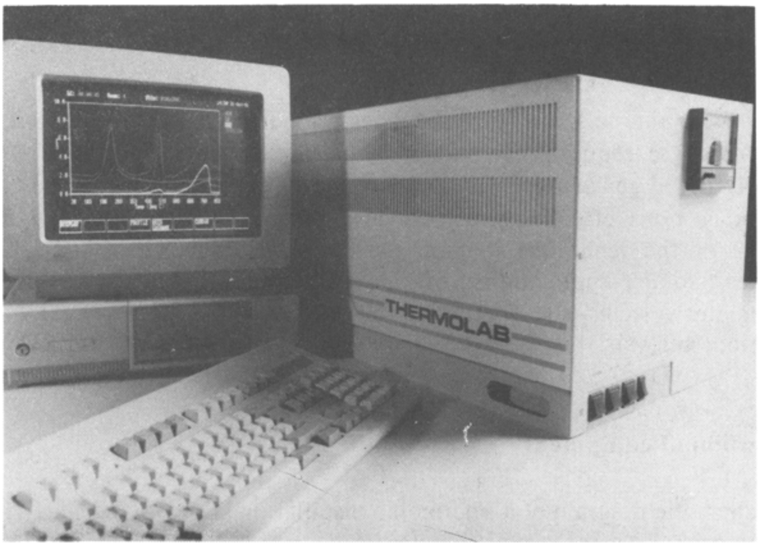

Fig. 2 The Thermolab

Mass spectrometer

The 300 amu range analyser is fitted with a remote enclosed ion source for enhanced sensitivity, and an electron multiplier detector with a dynamic range of 10^7. A Faraday cup detector, which has excellent long-term stability, is also fitted for automatic calibration of the multiplier sensitivity. Mass range calibration is accomplished by admitting perfluorotributylamine vapour through a membrane inlet. The analyser is contained in an extruded aluminium housing which has been designed to give easy access for maintenance. The housing is evacuated by a turbomolecular pump (60 ls^{-1}) which can achieve the working vacuum in about one hour.

Interface

When using a mass spectrometer for EGA, some means of pressure reduction is necessary from atmospheric pressure in the thermal analysis unit to the high vacuum in the ion source. Gas is withdrawn at about 15 cm^3min^{-1} from the sample chamber through a flexible, heated, silica-lined steel capillary, some 1.2 m long, which effects the first stage of pressure reduction and also allows convenient positioning of the Thermolab relative to the thermal analysis unit. The final pressure reduction is made by means of a molecular leak (a silicon carbide frit) shown in Fig. 1. The absence of metal parts in the gas path allows acid gases, such as HCl, to be transmitted efficiently. An indication of the speed of response and sensitivity of the sampling system may be gained by consideration of the sharp EGA peaks shown in Fig. 3, which are due to the release of bubbles of CO_2 from a molten glass. 100 mg of the glass was heated at 20°deg·min^{-1} under nitrogen; the weight loss over the region shown was only about 0.01%.

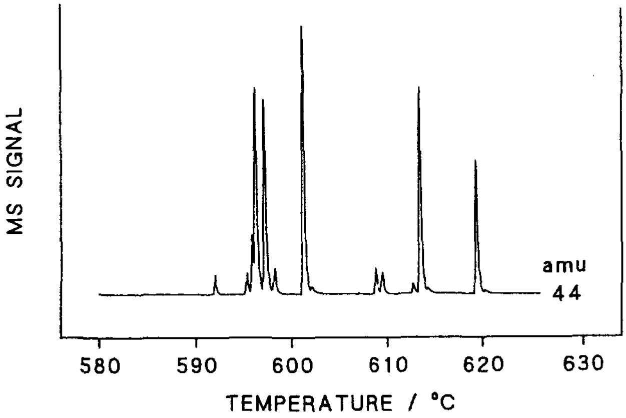

Fig. 3 EGA curve (CO_2) for a molten glass (sample weight, 100 mg; heating rate, 20 deg·min^{-1}; atmosphere, nitrogen)

Control and data processing

All instrument functions are controlled by a PC-compatible computer. The Thermosoft software also collects and analyses data. Several modes of data collection are possible, but two are used almost exclusively. The first is termed *log histogram* mode, in which complete mass scans are recorded over chosen mass and sensitivity ranges during the experiment, and is particularly useful in the examination of unknown volatile products. The software then allows up to six selected ions to be plotted as a function of time. Once the products have been identified, up to 16 chosen mass numbers may be followed continuously in the *multiple ion monitoring* mode with extremely high resolution. This latter method was used in the present studies. Data output is to a printer and/or HPGL-compatible plotter.

Thermal analysers

The Thermolab has been successfully connected to a wide range of instruments; the two used in the present studies were a DuPont 951 thermobalance, and a Stanton Redcroft STA 1500 TG-DTA unit. Details of the capillary connections to these have been described previously [1].

Data handling

The figures in this paper were created using the scientific graphics programme *Fig. P*, Version 6.0 (Biosoft), from ASCII files generated by the Thermolab and thermal analysis units.

Applications

The influence of molybdenum trioxide on the decomposition of PVC

EGA by mass spectrometry has been applied to a wide range of problems in polymer science [2, 3]. The materials studied here were a fully-formulated PVC containing plasticiser and anti-oxidant, either with, or without, the addition of 4% by weight of molybdenum trioxide, which confers smoke-suppressant qualities on the burning polymer [4]. The materials, in the form of pellets of about 30 mg, were heated at 20 deg·min^{-1} under nitrogen. The mass spectrometer was used to monitor a number of products, including benzene at 78amu. Before and after each thermal analysis experiment, benzene was introduced via a septum inlet into the purge gas stream by means of a microlitre syringe, to allow quantification of the benzene released by the polymers. Figure 4 shows the TG and EGA curves for the two formulations. The addition of the MoO_3 has modified the course of the decomposition of the PVC, as evidenced by the TG curves, while the EGA curves show that the quantity of benzene released has been markedly reduced. Comparison of the EGA curve peak areas obtained from the samples and the benzene standards gave estimates of 0.1 and 2.1% by weight of benzene released from the samples with and without MoO_3 respectively. The benzene (and other aromatics, which are the precursors of smoke) is believed to arise from the cyclisation of fragments of the highly conjugated residue remaining after the loss of HCl, which is the principal product of decomposition. Since MoO_3 is a *cis/trans* isomerisation catalyst, a higher proportion of these fragments exist in the *trans* conformation and are unable to effect ring closure.

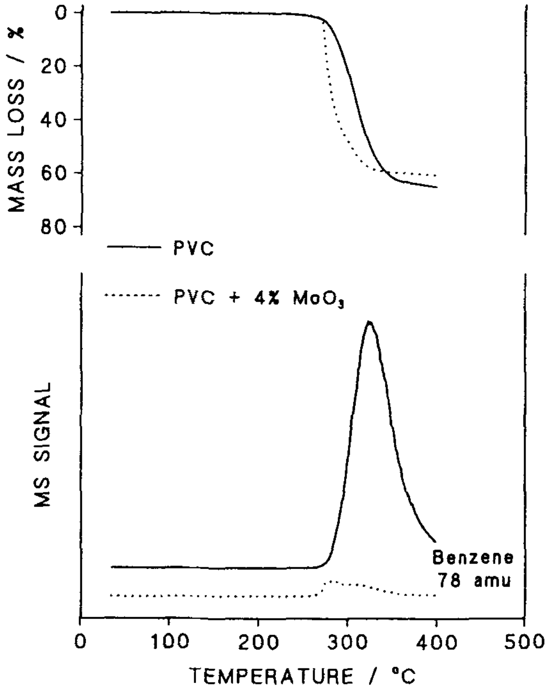

Fig. 4 TG and EGA curves for a PVC sample with and without MoO_3 (sample weight, 30 mg; heating rate, 20 deg·min^{-1}; atmosphere, nitrogen)

Assessment of the catalytic activity of modified clays

The EGA method described here offers a rapid means of assessing the relative activity of catalysts. The sample used was a Texas montmorillonite which had been treated with hot 30% H_2SO_4, washed and dried. The treated material is known to act as a catalyst for the dehydration of alcohols [5]. After exposure to propan-2-ol vapour at room temperature for several days, a 16 mg portion of the clay was heated at 10 deg·min^{-1} under nitrogen. The mass spectrometer was used to monitor ions specific to the propan-2-ol (31 amu) and the products propene (39 amu) and water (18 amu). The TG curve (Fig. 5) shows only a single weight loss, which is seen from the EGA curves to be a result of overlapping processes. Initially propanol and adsorbed water are evolved, while at higher temperatures the products propene and water are lost. The relative sizes of the peaks for propene and propanol gives a measure of the activity for a series of preparations.

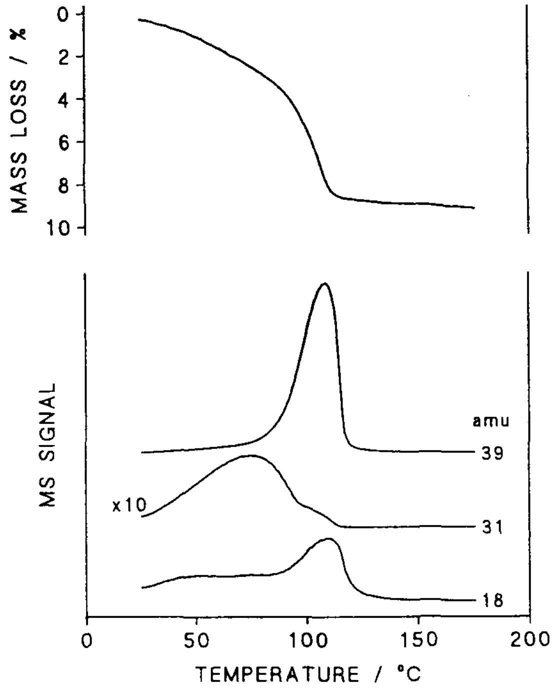

Fig. 5 TG and EGA curves for an acid-treated montmorillonite with adsorbed propan-2-ol (sample weight, 16 mg; heating rate, 10 deg·min^{-1}; atmosphere, nitrogen)

Examination of brick clays

A review of the use of EGA in mineral studies has been published [6]. The example chosen here is of an Oxford clay (supplied by D. J. Morgan, British Geological Survey) used in the manufacture of common bricks. The presence of certain constituents in such clays in large amounts is undesirable: carbonates may affect plasticity and increase porosity; pyrite and carbonate together may produce surface defects on exposure of the finished product; pyrite with organic matter can produce bloating (swelling) and black-coring. The suitability of clays for this purpose is conventionally assessed by physical testing, but information from TG-MS experiments can offer a more detailed chemical characterisation of the firing process. A 40 mg portion of the clay was heated in air at 20 deg·min^{-1}, while monitoring water (18 amu), carbon dioxide (44 amu) and sulphur dioxide (64 amu). The TG curve in Fig. 6 shows a multi-stage weight loss extending to high temperatures, which may be interpreted by use of the EGA curves. The lower curve shows peaks due to the loss of water from clays and gypsum below 200°C. The sharp peaks on all the curves at about 300°C arise from the combustion of volatiles from the degradation of organic matter. The higher temperature processes – dehydroxylation of clay minerals, the oxidation of pyrite, oxidation of residual carbon from the organic matter, and dissociation of calcite – are all clearly revealed on the EGA curves.

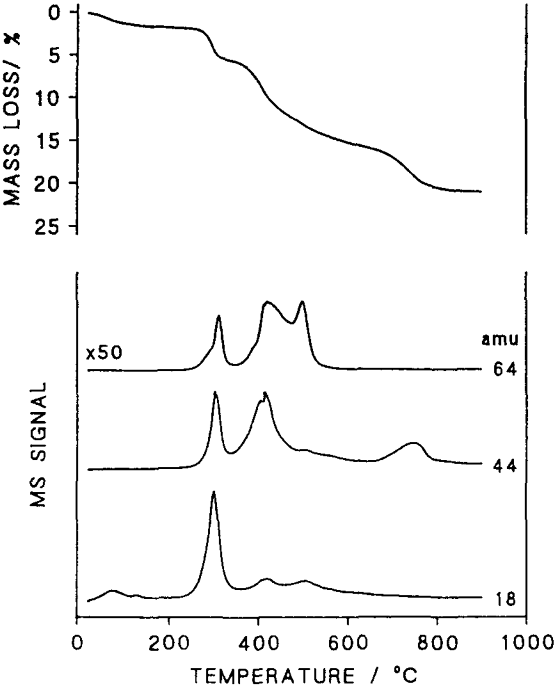

Fig. 6 TG and EGA curves for an Oxford clay (sample weight, 40 mg; heating rate, 20 deg·min^{-1}; atmosphere, air)

Pyrotechnics

Some applications of TA-MS to pyrotechnics have been described previously [1]. The present example is taken from a study of a titanium-strontium nitrate-Alloprene composition [7]. The DTA curve for this system shows a small initial exotherm around 300°C which was shown to be crucial to the overall ignition process. This is shown in Fig. 7, together with the TG curve, and EGA curves for NO, HCl, CO_2 and NO_2. Nitrogen and water (not shown for reasons of clarity) were also evolved. The EGA curves, supported by chemical analysis of the reaction products, have allowed the following reaction scheme to be established.

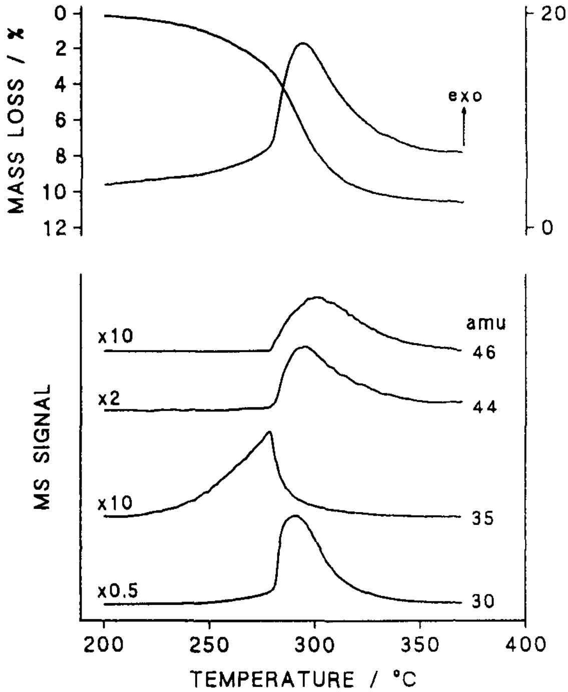

Fig. 7 TG, DTA and EGA curves for 44% titanium a – 44% strontium nitrate – 12% Alloprene composition (sample weight, 20 mg; heating rate, 10 deg·min^{-1}; atmosphere, argon)

1) Alloprene (a chlorinated rubber) decomposes above 200°C to release HCl:

$$(C_{10}H_{11}Cl_7)_n \rightarrow \text{"carbon"} + HCl$$

2) Part of the HCl reacts with strontium nitrate:

$$Sr(NO_3)_2 + 2HCl \rightarrow SrCl_2 + 2NO_2 + 0.5O_2 + H_2O$$

$$NO_2 \leftrightarrows NO + 0.5O_2$$

3) The oxides of nitrogen and oxygen oxidise part of the carbonaceous Alloprene residue largely according to:

$$1.5C + 2NO_2 + 0.5O_2 \rightarrow 1.5CO_2 + 2NO.$$

Some NO_2 escapes however, and some NO is reduced, accounting for the production of nitrogen. No oxygen was detected. Reaction (3) is responsible for the exothermic nature of the overall reaction, since the reaction between strontium nitrate and HCl was found to be endothermic; good agreement between the form and position of the CO_2 and DTA peaks may be observed. Quantification of the CO_2 released by means of an internal $NaHCO_3$ standard led to an estimate of 8% oxidation of the Alloprene residue.

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Zusammenfassung — Zur Untersuchung freigesetzter Gase wurde ein unlängst, speziell für die Thermoanalyse entwickeltes Quadrupol-Massenspektrometer an eine Thermowaage und ein simultanes TG-DTA-Gerät angeschlossen. Anhand von Beispielen aus vier Forschungsbereichen wurde die Arbeitsweise und die Einsatzmöglichkeit dieses Versuchsaufbaues erläutert.