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A NEW INTEGRATED SYSTEM FOR SIMULTANEOUS TG-DTA-MASS SPECTROMETRY

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SUMMARY

A new integrated TG-DTA-MS system is described based upon a simultaneous TG-DTA unit coupled to a 200 amu range microprocessor-controlled quadrupole mass spectrometer. An inert sampling facility and bakeable dual inlet system allow runs to be performed in a wide range of atmospheres, at temperatures up to 1500°C.

INTRODUCTION

Thermal analysts have long recognised the necessity for supplementary information in the interpretation of complex thermoanalytical curves. Simultaneous methods are generally accepted as providing this information in the most reliable and meaningful way, as it is obtained from a single sample under the same conditions. A major technique for complementing the power of simultaneous TG-DTA is evolved gas analysis, and this can be most effectively performed using the sensitive and versatile mass spectrometer.

Our aim in constructing the Stanton Redcroft TG-DTA-MS instrument has been to provide an integrated system which is easy to use, compact and relatively inexpensive, while retaining the features of fast scanning speed, sensitivity and versatility required for high performance thermal analysis.

DESCRIPTION OF THE INSTRUMENT

A block diagram of the complete apparatus is shown in Fig.1. The heart of the system is the STA 781 simultaneous TG-DTA unit, operating up to 1500°C, with heating rates up to 50°C min^{-1} (ref.1). The balance has a noise level of a few microgrammes and a negligible buoyancy correction under most conditions. The plate-thermocouple DTA head enables quantitative performance to be obtained with good sensitivity and resolution.

The STA 781 has a special feature which renders it ideal for EGA - an alumina cup within the furnace which surrounds the measuring head (Fig.2). The small swept volume, about 4 cm^3, which this produces, minimises dilution of products in the purge gas and increases

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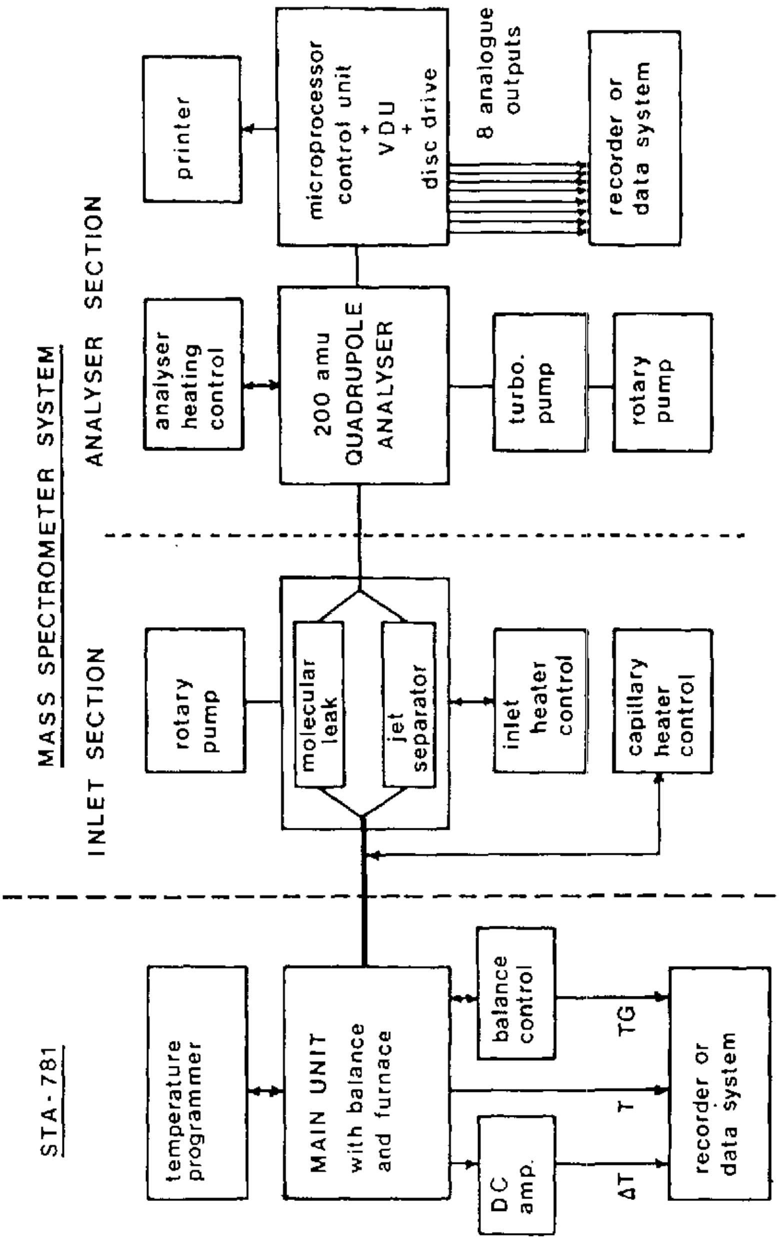

Fig.1. Block diagram of simultaneous TG-DTA-MS system.

sensitivity of detection. The high purge rate, typically $50cm^3min^{-1}$, preserves the resolution of closely-spaced thermal events. Some 10 cm^3min^{-1} of the purge gas/product mixture is drawn into the alumina tube which takes it from the hot zone of the furnace; thereafter it passes to the mass spectrometer via glass-lined stainless steel tubing. This tubing is heated to about 180°C to prevent condensation, and the glass lining minimises adsorption, corrosion, or catalytic degradation of sensitive organic species. The time between generation of the gaseous product and registration by the analyser is less than one second.

The pressure reduction between ambient pressure in the STA 781 and 0.1 mPa in the MS analyser may be effected by either of two interfaces. A molecular leak and a jet separator are mounted in parallel in an oven controllable up to 200°C. The molecular leak may be operated with any common purge gas, and thus the conditions of the thermal analysis experiment are not compromised. The jet separator provides a major increase in sensitivity, but must be operated with a helium or hydrogen purge gas.

The mass spectrometer itself is a 200 amu range microprocessor-controlled unit made by VG Quadrupoles Ltd. The vacuum system is pumped by a fast, clean turbomolecular pump capable of achieving working pressure in about one hour from switching on. The entire analyser is also mounted in an oven so that background signals are reduced to a minimum, allowing better detection limits for water and carbon dioxide in particular. Two detectors are provided - a Faraday cup for calibration and precise quantitative work, and an electron multiplier for fast scanning and higher sensitivity.

The instrument, which possesses extensive and easy to use software, may be operated in the scanning mode for identification of unknown products. The spectra may be viewed on the integral VDU before copying to a printer. The scan speeds are typically of a few seconds for the entire 200 amu range. Many spectra may thus be recorded during a weight loss process. The most useful facility for thermal analysis, however, is the "peak select" mode, in which up to 8 gases may be continuously monitored as a function of time. Signals corresponding to these are passed to a recorder or data system. Evolved gas profiles are thereby generated simultaneously with the TG, DTG and DTA records, and aid greatly in their interpretation, both qualitatively and quantitatively.

The entire MS unit is mounted in a compact cabinet 1.4 m in height, fitted with castors to enable easy location adjacent to the STA 781 unit. Careful layout and the incorporation of cooling fans allow the instrument to run without the need for water circulation and only a

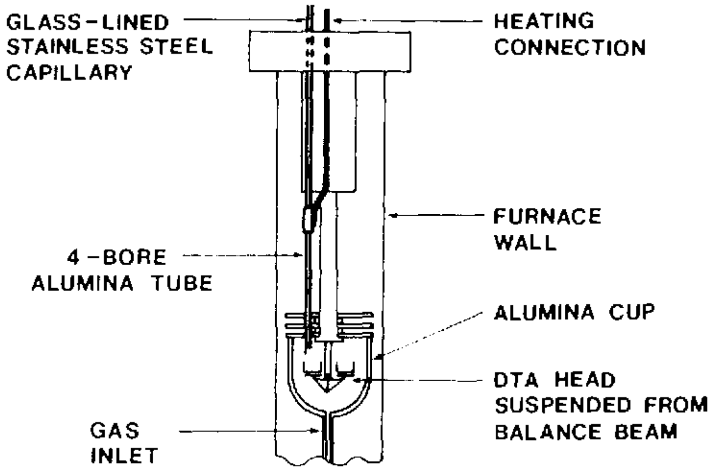

Fig.2. Cross-section of STA 781 gas sampling system.

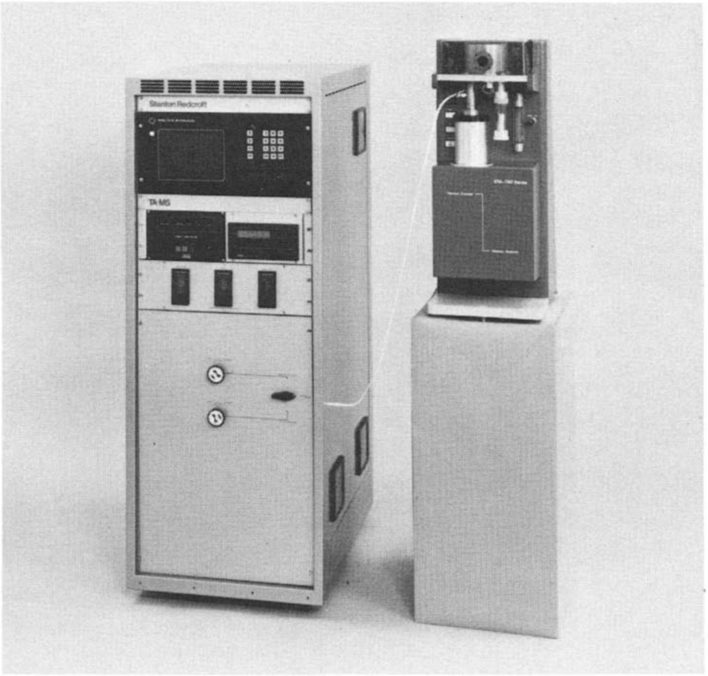

Fig.3. Photograph showing simultaneous TG-DTA-MS apparatus.

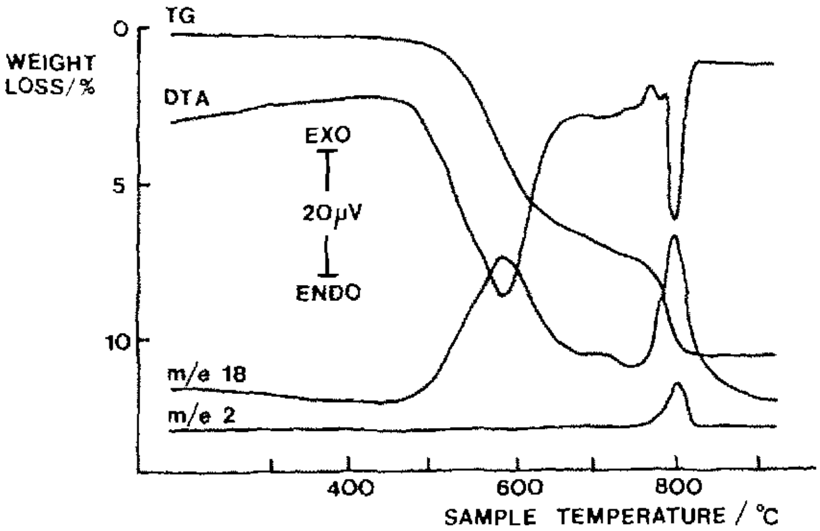

Fig.4. TG-DTA-MS curves for ripidolite.
(30mg, 20°C min^{-1}, nitrogen)

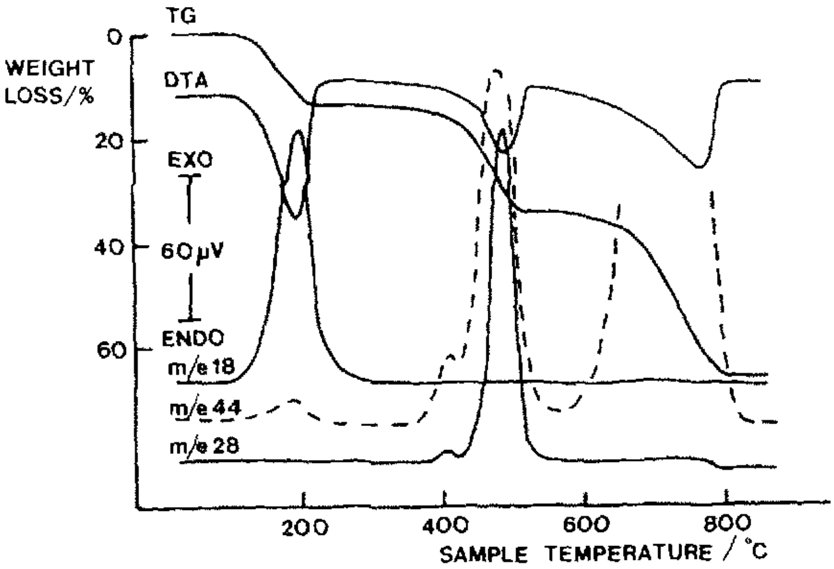

Fig.5. TG-DTA-MS curves for calcium oxalate monohydrate.
(15mg, 15°C min^{-1}, argon)

single power connection is required. A photograph of the STA 781 and mass spectrometer modules is shown in Fig.3.

APPLICATIONS

The first stage in the examination of a material of unknown thermal behaviour would be to perform a TG-DTA experiment, while recording sequential mass scans during any weight loss stages. The gaseous products thereby identified may then be monitored continuously in a second experiment in the "peak-select" mode, which has inherently higher sensitivity and reveals more detail of the course of the decomposition process.

An example of the type of information generated by the TG-DTA-MS system is shown in Fig.4 by the simultaneous thermal curves of ripidolite, an iron-rich chlorite. In the inert atmosphere used here, Fe(II) exposed after or during the first water loss, has reduced evolved water to hydrogen in the second stage. The exact features of the curves are heavily dependent on experimental conditions, particularly sample preparation. It is therefore advantageous to apply multiple simultaneous methods to allow sensible interpretation of the thermal behaviour.

Fig.5 shows the results of a run in argon on the familiar example of calcium oxalate monohydrate. The conventional interpretation of the decomposition ascribes the successive weight loss stages to the evolution of water, carbon monoxide and carbon dioxide. The high sensitivity used for the carbon dioxide trace shows some to be generated during the dehydration stage, which is possibly due to impurities in the sample. The carbon dioxide seen in the second weight loss stage is most probably due to disproportionation of the monoxide, as carbon is found in the final oxide residue.

ACKNOWLEDGEMENTS

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