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A LIMITED BUDGET APPROACH TO TG/MS

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For many years the main support analysis for thermogravimetry was centred on the qualitative and quantitative analysis of solid decomposition products. In general, the monitoring of gaseous effluent from the thermobalance has proved far more difficult.

The use of Katherometer detectors can provide useful information, particularly if the evolved gas is known, a gas density detector may also provide some degree of qualitative analysis. The coupling of gas chromatographs to thermobalances has proved successful, but is generally used when the volatile decomposition products from a reaction are known, and the chromatographic parameters can be adjusted in order to monitor these quantitatively. When the volatile components are not known, then it is desirable to identify these before a quantitative determination is attempted.

The usefulness of mass spectroscopy for identification of unknowns has been recognised for some time; one of the earliest utilisations of this technique in thermal analysis [1] involved a thin film of polystyrene deposited on quartz, and heated next to the inlet leak of a magnetic mass spectrometer. The temperature was elevated in small stages, recording mass spectra at each temperature. Decomposition began at 230°C and the sample was heated to 330°C over a period of 10 days.

There are two main problems encountered when thermogravimetry-mass spectrometry is considered. One is the capital outlay involved, the other is the technical problems involved in coupling a thermobalance, operating at atmospheric pressure, and having a flow of carrier gas of possibly 100 $cm^3\ min^{-1}$, to a mass spectrometer at 10^{-6} Torr.

It would be difficult, in many cases, to justify the high capital costs of a mass spectrometer capable of detecting volatile fragments over a wide molecular mass range with high resolving power. For a large number of decomposition reactions, the volatile fragments will consist of molecules of low molar mass. Indeed, high molar mass fragments are likely to prove difficult to sweep from the thermobalance, through the interface, to the mass spectrometer without condensation at some point in the system.

In the thermal decomposition of Group II metal salts of sulphonated propanone [4] all fragments were found below 100 atomic mass units, and for aromatic polyamide [2] the largest volatile fragment identified was diphenyl with mass 154.

A mass spectrometer is available at considerably lower cost than the high resolution, high mass range spectrometers generally available. The Kratos MS10S package (Fig 2) has a 5 cm radius analyser, with 180° deflection in a magnetic field of approximately 1.8 K gaus supplied by a permanent magnet. The scanning of up to 200 atomic mass units being carried out by means of a ramping accelarating voltage. Another possibility is the acquisition of a second hand mass spectrometer at reasonable cost, bringing qualitative and semi-quantitative evolved gas analysis within the analyst's budget.

Having overcome the economic problems we have now to challenge the interfacing. In 1960, Murphy et al [3] resolved this problem by placing a DTA sample holder and furnace in a bell jar (Fig 1), the system evacuated and samples allowed into collecting bottles at selected temperatures. These samples being removed and analysed by mass spectrometry. Obviously, this technique is not appropriate to dynamic atmosphere work, but provides a simple solution to the problem.

Three interfaces for continuous sampling of dynamic atmosphere thermogravimetry have been tried, between a Stanton vacuum and gas atmosphere mass flow thermobalance and either a Kratos MS10S or Hitachi RMU-6D mass spectrometer [4].

The first system employed 6 feet of 0.013 inch bore stainless steel capillary tubing connecting the thermobalance to a small sampling chamber which was evacuated by a rotary vacuum pump, allowing a small quantity of the gas stream to pass through a sintered disk leak to the mass spectrometer. This proved inflexible and prone to blockages when employed in evolved gas analysis, therefore a modification of this idea was developed.

The improved version used 4 mm internal diameter stainless steel tubing carrying the exit gas to an interface mounted as close to the mass spectrometer as possible. The interface (Fig 3) consisted of a 5 cm length of 0.1 mm bore glass capillary tubing leading to a small chamber, evacuated by a rotary vacuum pump, and containing a sintered disk leak to the mass spectrometer. Under a pressure gradient of atmospheric to 10^{-2} Torr the flow of air through the sinter was measured at approximately 1.5 cm^3 min^{-1}. This system proved far less prone to blockages and when this did occur, could be cleared very rapidly by the application of a gentle gas flame to the capillary. When linked to the Kratos MS10S this proved a simple, yet useful interface.

The gift from ICI Ltd, Billingham, England of an Hitachi RMU-6D mass spectrometer prompted the development of an alternative interface capable of

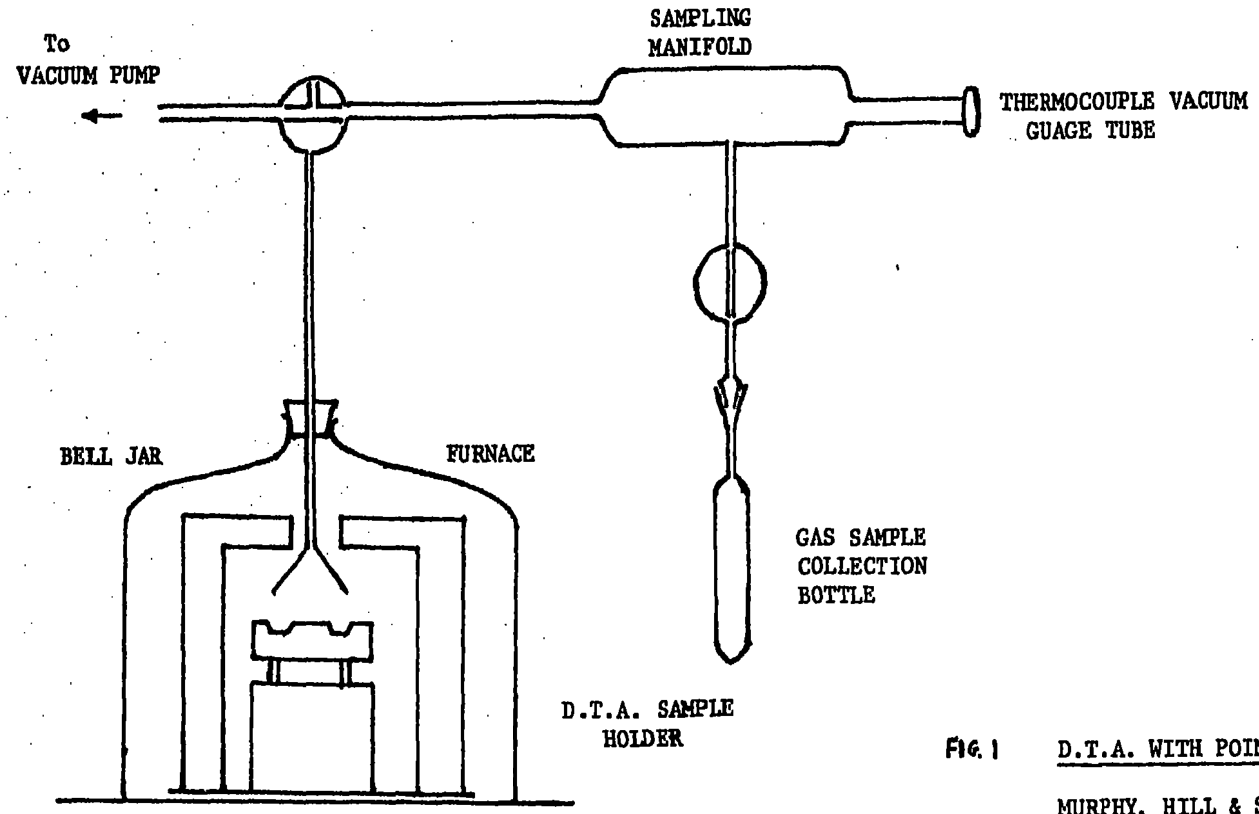
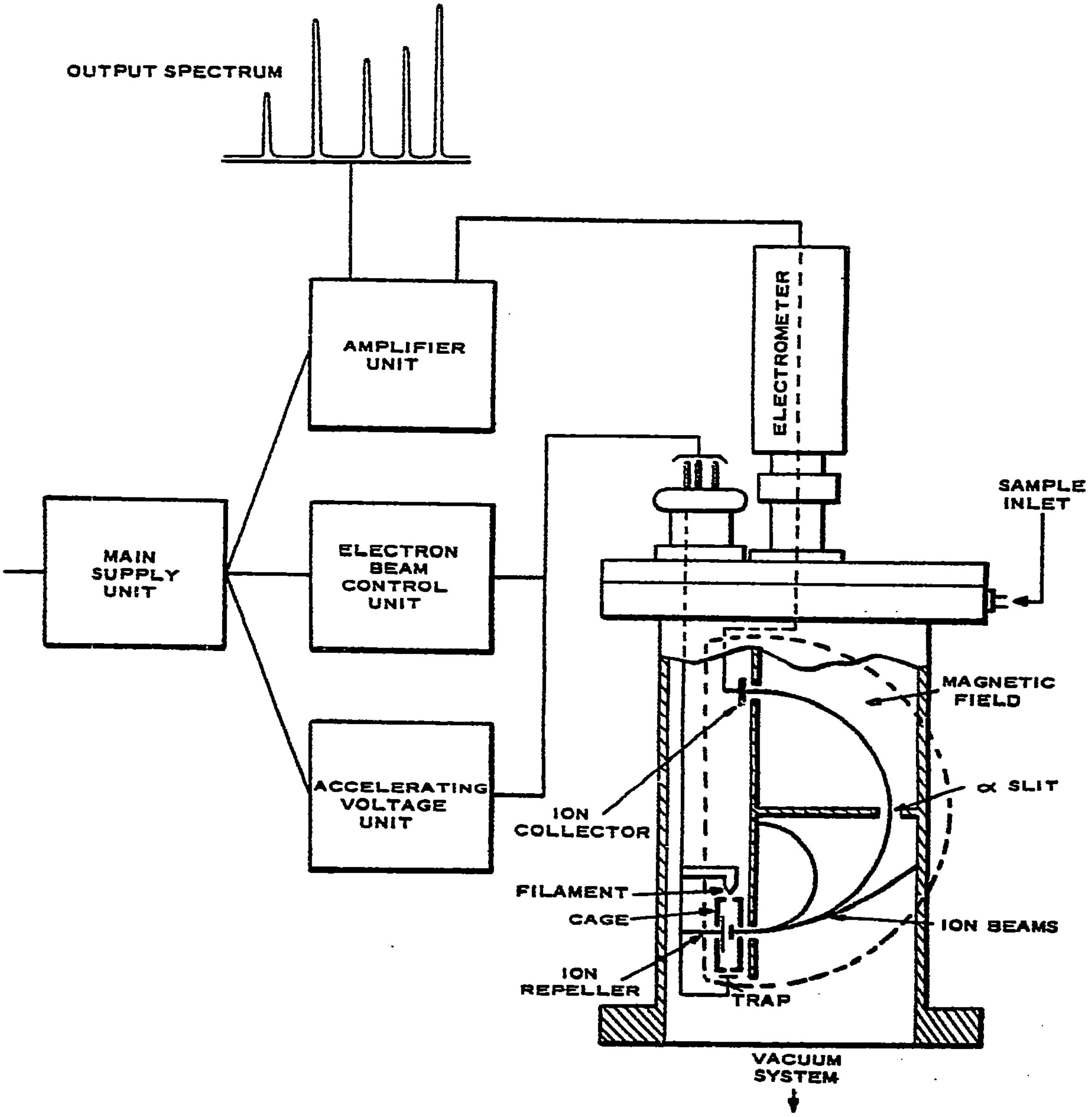


FIG. 1 <u>D.T.A. WITH POINT-BY-POINT SAMPLING</u>

<u>MURPHY, HILL & SCHACHER 1960</u>

SCHEMATIC ARRANGEMENT OF THE MS10 MASS SPECTROMETER FIG 2



handling a wider variety of gaseous sample sources, particularly gas chromatography. The thermal analysis was still carried out on the Stanton mass flow thermobalance, but employing a jet separator to strip a substantial quantity of the Helium used as carrier gas from the stream (Fig 4). In order to reduce the risk of accidental collapse of vacuum in the mass spectrometer fine capillary resistances were incorporated such that the maximum working pressure of the analyser could not be exceeded. The finely variable bypass valve and excess gas vent were present because the normal flow through the thermobalance was far in excess of the performance capabilities of the jet separator.

An alternative would have been to run a multistage separation system, ensuring a greater proportion of the evolved gases reaching the mass spectrometer, and hence improving sensitivity. The increased complexity of 'stacked' jet separators and associated vacuum pumps was not, however, required and another benefit of the simpler system is that elaborate precautions are not necessary to balance the gas flow through the thermobalance to the rate of evacuation of the pump.

There are commercially available jet separator interface systems for mass spectrometry:gas chromatography links. However, if earlier guidelines have been followed, this could prove to be a substantial fraction of the cost of the mass spectrometer. The alternative to this is a simple jet separator (Fig 5) which may be produced by a glassblower in a very short time for minimal outlay.

The fine tuning provided by the variable bypass valve ensures that the most suitable resistance to flow into the mass spectrometer may be selected to optimise conditions for the source of evolved gas to be analysed. When modern thermobalances of small size and low flow rate of carrier gas are coupled into this system, there may be little or no venting of excess gases. Under these conditions, precautions will have to be taken to ensure the gas flow balances the rate of evacuation, otherwise vacuum or pressure build up may occur. A positive pressure can easily be rectified, but under a vacuum build up there is a risk of contamination of the gas stream by air being drawn into the system.

The completed TG/MS system is capable of producing large quantities of data, and while it is possible to measure peak heights and plot ionic yield curves, if a large number of runs are envisaged then some form of data handling system might be considered. Once again, commercial units are available capable of handling this task, and will provide the easiest solution to this problem. If budget limitations rule this out there appear to be two alternatives.

Fig 3 By pass flow sampling

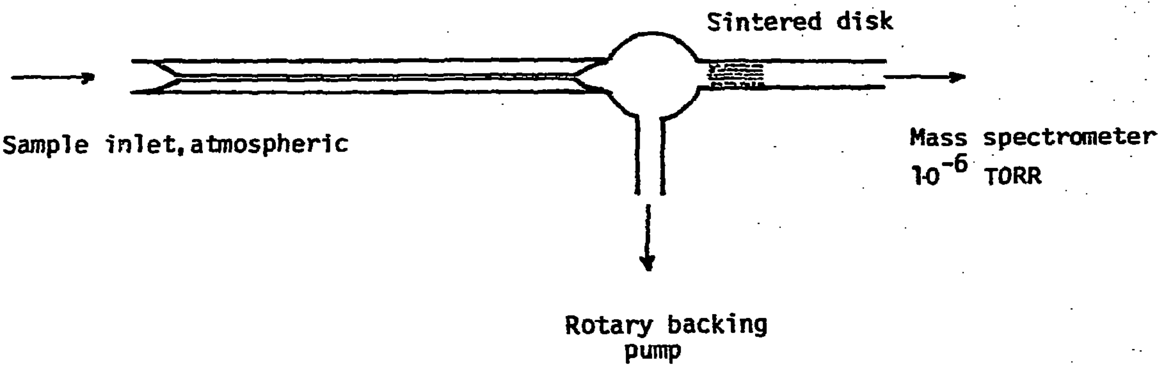
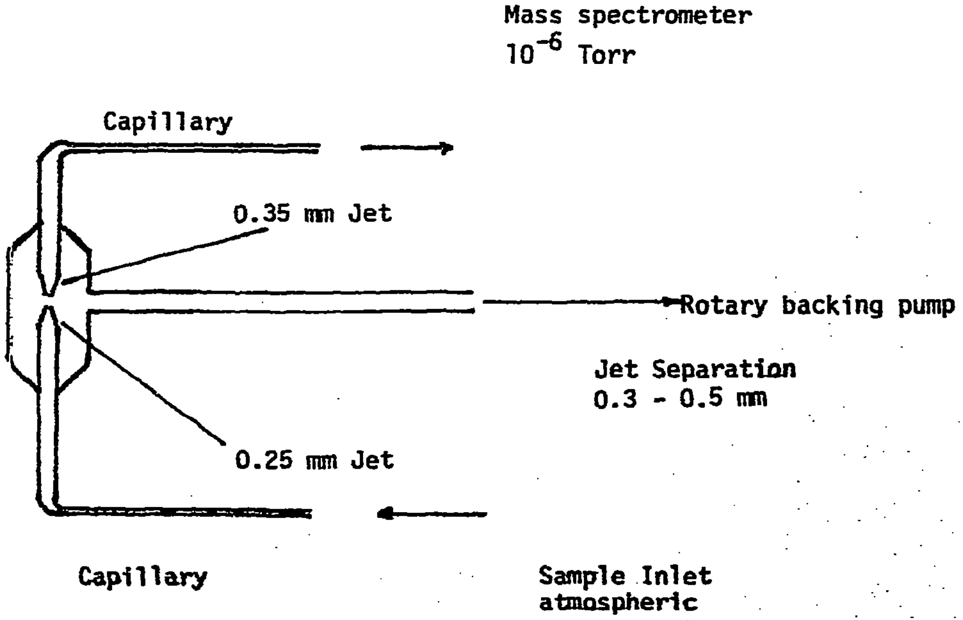


Fig 5 Jet Separator Interface



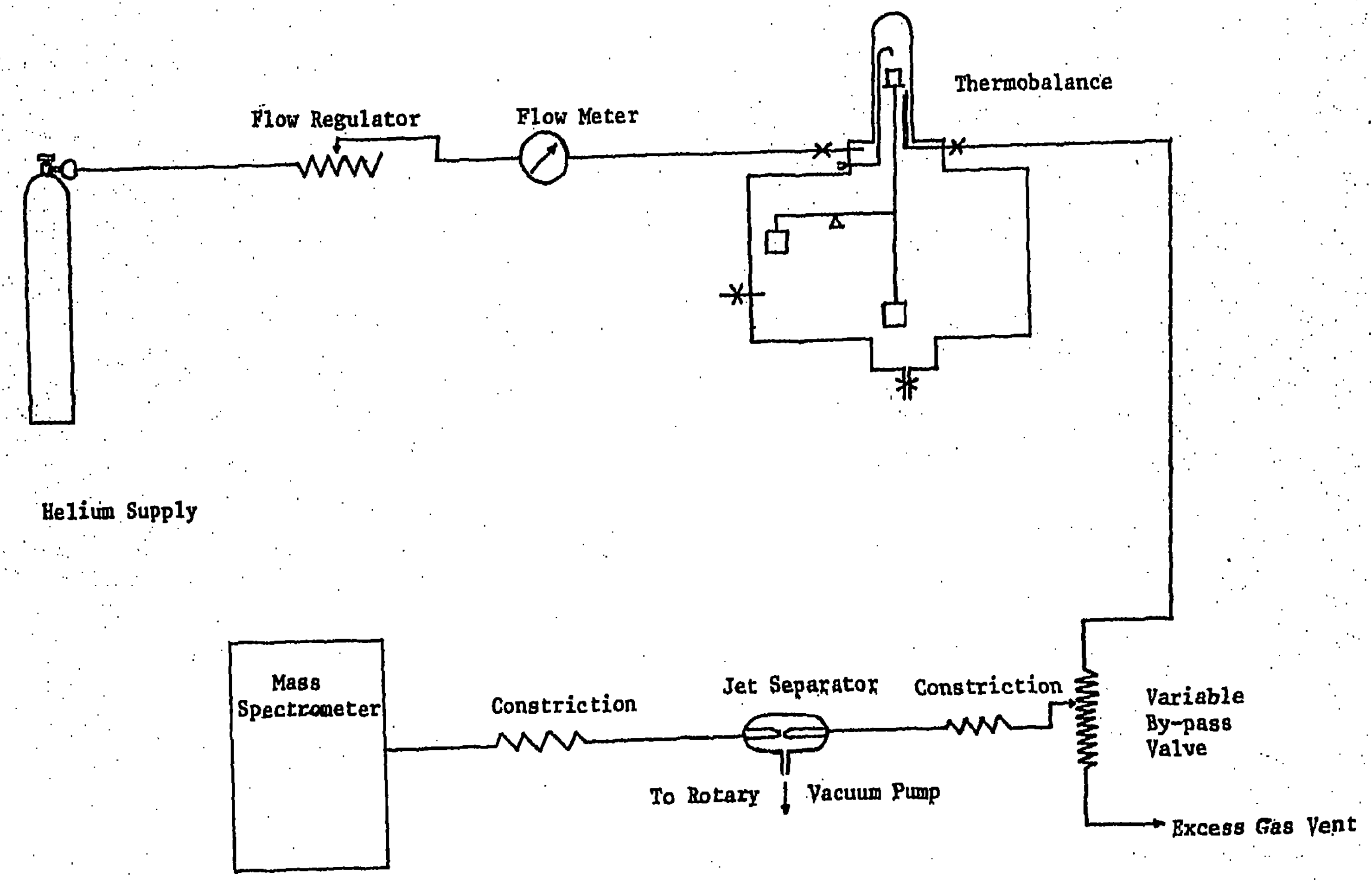
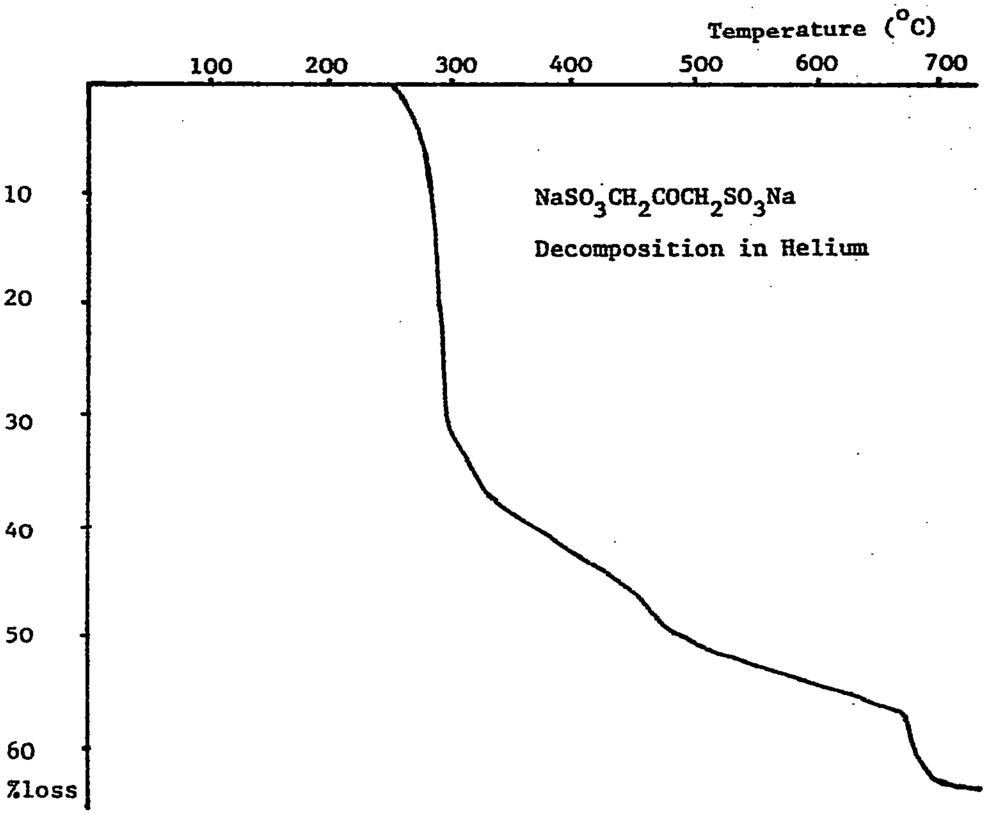


Fig 4 Thermogravimetry-Mass Spectrometry With Continuous Sampling



Main evolved gases, monitored by mass spectrometer

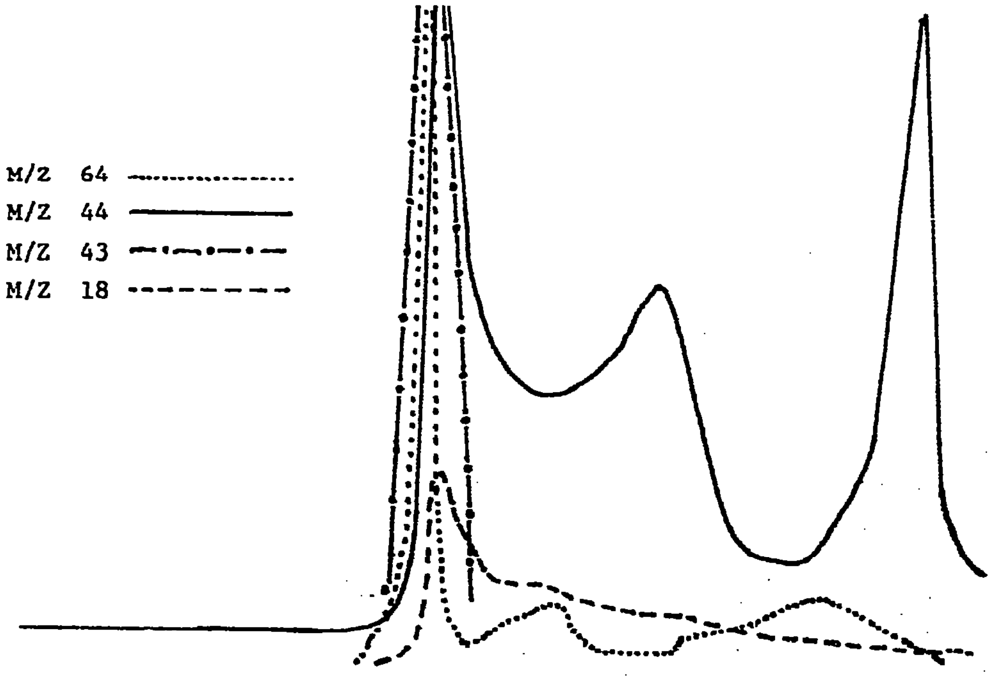


FIG. 6 T.G./M.S. Sodium Acetone Disulphonate

A system reported by Langer et al [5] for their DTA - time of flight mass spectrometer system involved feeding the signal from the electron multiplier into sampling oscilloscope equipped with a display scanner swept by a wave form generator acting as an external gate. The scan rate of 3-10 scans per second was gated, and the data recorded on an annalogue tape recorder, together with DTA and timing pulse. Playback via the oscilloscope with the gate adjusted for the time of appearance of a single ionic mass, and repeated for various different masses could yield a series of ionic yield curves.

With a low resolution mass spectrometer it is possible that with the addition of an annalogue to digital converter, and writing suitable software, this task could be carried out on one of the many minicomputers available. This approach has been tried with the Kratos MS10S system and CBM 'Pet' computer and while the project was never completed, it did demonstrate that, with machine code sampling, it was perfectly capable of reading peak crests produced by the mass spectrometer. With higher resolution spectrometers extremely fast sampling is required in order to find the peak crest, and something more sophisticated than a CBM 'Pet' is required.

A simplified example of what may be achieved by hand is shown in Fig 6, where heights of mass spectral peaks of interest are measured and plotted against temperature.

The use of mass spectrometry in evolved gas analysis is not compatible with the use of oxygen as the purge gas through the thermobalance, as this causes drastic reduction in the life of the ion source filament, but most other gases can be used. There are advantages to the use of helium as purge gas;being easily stripped from the gas stream to enrich the sample, difficult to ionise (the total ion count may be used as an indication of the quantity of evolved gas reaching the analyser), and having a mass low enough not to interfere with the spectra.

The expense of mass spectrometry for evolved gas analysis need not be so high as to remove the technique from the analyst's reach, and there are many ways of solving the interface problems only a few of which have been mentioned here. TG/MS on a 'shoe string' can be a very useful tool which deserves much more exploitation.

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