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MASS SPECTROMETRIC EVOLVED GAS ANALYSIS—AN OVERVIEW

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ABSTRACT

The uses of mass spectrometric evolved gas analysis systems have been described and discussed in relation to solid state reactions giving rise to gaseous products. Emphasis has been placed on the use of such systems for kinetic studies. The theoretical considerations necessary to ensure quantitative and linear results have been described.

INTRODUCTION

The use of modern analytical techniques to study the individual characteristics of gases evolved from a solid during heating is more conducive to the understanding of thermal decomposition reactions than techniques involving overall accumulatory pressure measurements [1]. The latter, in common with mass loss measurements, usually refer to the total chemical change within a system. However, when there are several products it is most desirable to be able to differentiate between those products and to investigate progressive changes in gas composition.

The most widely applied techniques of evolved gas analysis (EGA) have been mass spectrometry (MS) and gas chromatography (GC). Both allow qualitative and quantitative measurements to be made but, because it employs batch sampling, the GC technique is significantly slower in operation. Also, thanks to the increased automation and hence simplicity of use, general purpose MS systems are being applied more frequently.

In this article we describe firstly the many methods available for using MS

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in evolved gas analysis. Secondly, the exploitation of MS–EGA systems in kinetic studies is discussed.

EARLIER REVIEWS

The use of MS–EGA systems up to 1969 in kinetic and mechanistic studies has been reviewed by Korobeinichev [2]. He noted that the effect of gas sampling from the sample system into the EGA equipment for the purposes of a kinetic study must be either to remove all the product as it is formed or to remove a negligible amount. Anything in between requires very complex mathematical treatment to allow for gas flow rates through a sampling valve or capillary at varying pressures and diffusion coefficients. The few papers he lists as having derived kinetic parameters from MS–EGA systems have done so using methods which ensure that the rate of gas evolution is very much smaller than the rate of gas withdrawal into the MS analyser. They assumed that the peak height of a particular mass studied was proportional to its rate of evolution and so were able to calculate Arrhenius parameters. However, the majority of work described by Korobeinichev seeks to elucidate the mechanism of complex multistaged degradation reactions.

Friedman [3] has reviewed MS–EGA up to 1970 and although he has listed many examples of the use of the technique these do not include kinetic studies. The major use of the technique from his viewpoint is the elucidation of structure and composition of unknown samples. Wendlandt [4] in a broader review of all the types of EGA systems included work up to 1974.

Risby [5] reviewed the use of MS–EGA systems for the characterisation of biological and biochemical materials up to 1978. MS–EGA based methods of sample characterisation have one main advantage over conventional MS analysis. Often the interpretation of mass spectra resulting from compounds of exceptionally large molecular weight is either very difficult or impossible due to the complexity of such spectra. If, however, the compound is thermally broken down in a controlled way to give a series of volatile products then structure elucidation is improved.

Eppler and Selhofer [6] reviewed simultaneous TG/quadrupole MS systems. They described the different methods used to couple the two techniques but did not examine the quantitative nature of these.

The following discussion draws on selected examples from the aforementioned reviews as well as work published since 1973 in order to illustrate the variations possible. The use of the technique is now very widespread and so only recent work showing significant developments and improvements is described.

METHODS INVOLVING TOTAL GAS SAMPLING

Removal of all the gaseous decomposition products into the MS analyser is best achieved by placing the sample within the MS itself. This was done by Langer and Gohlke [7] in one of the earliest examples of MS–EGA. They heated samples in a miniature furnace located within the ion source of a time-of-flight MS and were thus able to correlate DTA peaks with particular gaseous evolutions. Similar work has been published by Dubrovin et al. [8–10] who studied the reaction mechanism of uranium acetate decompositions. They also plotted $\ln(d\alpha/dT)$ against $1/T$ and calculated the activation energy from the gradient. Gallagher [11] used a similar system with a quadrupole MS in a mechanistic study of zinc and oxygen loss from several ferrites on heating. Wilson and Hamaker [12] built a high vacuum microbalance into the heart of a quadrupole mass analyser for polymer degradation studies. All these types of systems have the advantage that, due to the short sample–analyser distance involved, secondary reactions involving the true product gases leading to erroneous interpretations are minimised. Thus, Price et al. [13,14] in a development of work by Shulman and Lochte [15] were able to heat barium nitrate and follow the evolution of NO, NO_2 and O_2 gases which have proved difficult to quantify with other systems. Experimentally they used a time-of-flight MS analyser incorporating a miniature furnace in the source region. They also used the system to calculate kinetic parameters for the rising temperature decomposition of cadmium carbonate.

An alternative method of ensuring that all gaseous decomposition products enter the MS analyser is to connect the sample system directly to the spectrometer using a system of connections designed to introduce as few obstacles to the gas flow as possible. This type of system was used by Ryska [16] for the analysis of the products of polymer degradation. The advantage these systems have is that, if large amounts of product gases are likely to be produced so overloading the MS analyser, it is fairly straightforward to build a pump into the sample system. Such a system, using a vacuum thermobalance, has been described in detail by Wiedemann [17] and successfully used by many others [18–21] to study a range of samples. These include polymeric [19], inorganic [20] and geological [21] materials. Variations on this basic type of system have been developed. For example, Baumgartner and Nachbauer [22] have discussed the use of a chemical ionisation MS (CIMS) which they linked to a TG unit via a metering valve in a similar way to that described by Wiedemann [17]. CIMS has the advantages of ease of interpretation and of being able to operate at higher input pressures, so allowing larger sample sizes to be used. The thermal decompositions of calcium oxalate hydrate, copper tetrammine sulphate hydrate, and potassium trifluoroacetate were studied this way.

Providing that the flow conditions that exist in any of the aforementioned systems are understood then the degree, α, and rate of decomposition with respect to time, t, or temperature, T, can be accurately calculated. Shulman and Lochte [15] discussed the case where the sample is heated within the MS analyser. They state that the fractional decomposition can be calculated from the ion current measured for a characteristic mass spectral ion. This is because the current is taken to be proportional to the rate of gas evolution which in turn is proportional to the rate of the mass loss of the sample. Thus, at any point on the ion current curve the degree of decomposition is equal to the value of the area up to that point divided by the total area. Therefore an $\alpha - T$ or $\alpha - t$ plot can be constructed enabling the Arrhenius parameters to be calculated. This method assumes that the flow of evolved gases from the sample to the ionisation region of the MS analyser is instantaneous and so the gases are not able to fractionate prior to analysis. However, this method is seldom used, MS–EGA being mainly used for qualitative work.

The main disadvantage of the systems discussed so far is that they all restrict the environment of the sample to that of a vacuum. As mentioned earlier other environmental conditions require the use of a gas sampling system. These are discussed below.

METHODS INVOLVING SELECTIVE GAS SAMPLING

One of the earliest examples of an MS–EGA system capable of studying decomposition reactions occurring in non-vacuum conditions was described by Wendlandt and Southern [23]. They conducted their experiments in a flowing inert atmosphere and led the effluent gases via a katharometer detector to the molecular leak inlet of an MS. A limitation of their system was the scan time of the MS analyser which was three and a half minutes. A long scan time can lead to distorted mass spectra from a rapidly changing effluent gas stream unless care is taken. It was possible however for Wendlandt and Southern to monitor one mass peak continuously as a function of time. Using this latter technique they studied the thermal decomposition of copper tetrammine sulphate hydrate. Similar work was done by Zitomer [24] who used a metering valve as a bypass between an MS analyser and flowing gases within a commercial TG unit. He used the system to study the thermal degradation of polymeric materials. Baker [25], also using this technique, placed a capillary bypass between the furnace and a quadrupole MS in a study on the pyrolysis of tobacco. He was able to conduct kinetic and mechanistic studies using this method although he did not calculate Arrhenius parameters.

The primary use of these systems has been to enable products giving rise to particular DTA peaks and TG curves to be identified [26–31]. Morisaki [32] in a variation on this technique placed a gas chromatograph between the TG system and the MS analyser so separating products which were then identified by MS. This method enabled him to study the pyrolysis of fluorocarbon polymers at different temperatures. This type of system was further developed by Buttler et al. [33]. Chiu and Beattie [34] placed traps in the evolved gas stream to remove high molecular weight residues prior to sampling by the MS analyser and so aid the analysis of the resultant mass spectra. Bracewell and Robertson [35] identified the products of pyrolysis of humus, admitted from a pyrolysis unit into the MS analyser via a leak valve. Similar work has been done using a narrow bore capillary as a bypass between the gas effluent stream from TG units and MS analysers [36–38]. Nambiar et al. [39] used a simple system to heat very small amounts of sample in a previously evacuated chamber to predetermined temperatures. The contents of the chamber were then admitted directly to an MS analyser for identification of the products.

Emmerich and Kaiserberger [40] developed two methods of interfacing a simultaneous TG–DTA unit to a quadrupole MS-analyser. The TG unit was able to operate under any atmospheric conditions. The first method of interfacing used a platinum capillary open at one end to the sample gases and at the other to a continuously pumped vacuum chamber. From here an orifice lead to the MS analyser. The second method used a ceramic tube with an orifice at one end in place of the platinum capillary. Both interfaces were claimed to be quantitative and capable of providing a gas throughput of unvaried composition. This is because the proportion of gases sampled is at such a pressure that viscous, laminar flow is ensured prior to entry into the MS analyser.

The qualities of the two system types, namely those operating with a high vacuum in both the TA and MS units and those with atmospheric pressure in the TA unit and high vacuum in the MS unit, have been compared by a number of workers. Szekely and Till [41] used a quadrupole MS analyser together with a TG unit. Two modes of connection were used, one involving flowing gas with a leak valve bypass into the MS analyser and the other involving direct coupling of the two units via a short wide bore tube operating under vacuum. They state that both systems were found to be suitable for analytical and kinetic purposes although they show no results to prove this. Freund et al. [42] studied the dehydration of magnesium hydroxide by MS–EGA. The samples were heated in a silica tube linked either directly to an MS analyser or indirectly to a capillary inlet. The results were found to be different but this was explained in terms of differences in the sample environment between the two experiments.

One of the main disadvantages of the latter technique of gas sampling is that, in general, of the gases admitted to the analyser the carrier gas is much the largest component. Thus, the evolved gases are often present as small fractions of the carrier leading to a dramatic loss of sensitivity. Also, for the purposes of kinetic studies it is difficult to ensure that the coupling system is linear and quantitative. An alternative to both systems is that provided by MS analysers incorporating jet separators as inlets. These devices enable evolved gases to be separated from a stream of flowing helium for direct insertion into an MS analyser. Barnes et al. [43] have described the coupling of DTA and TG units via a jet separator to a quadrupole MS. They describe the main advantage as being the fact that approximately 50% of the sample is transferred to the MS so leading to an increase in sensitivity of approximately 200 times. The system is described as being suitable for kinetic studies. Smith [44] has compared the results obtained using a jet separator with those obtained by heating the sample in a programmed probe within the MS source. The use of a programmed probe is widespread in the identification of organic solids which are vaporised within the MS at a temperature below their decomposition point. However, these probes can be used for the thermal decomposition of less volatile solids. Smith [44] concludes that the use of a jet separator has many advantages over other inlet systems although it is less sensitive than direct insertion techniques. The difficulty with programmed probe techniques is that very small sample sizes are required and thus any solid must be uniform. Sample masses of approximately 0.1 mg can be successfully used with jet separator methods thus making them more sensitive than other non-vacuum systems.

All the systems described so far fall into one of the two well defined groups described at the beginning of this section. However, Dollimore and co-workers [45,46] have described a system which is relatively simple but less readily defined. This consists of a vacuum microbalance connected to a large expansion bulb which in turn is connected via a calibrated slow leak valve to an MS analyser. Prior to the start of an experiment, the microbalance and expansion bulb were evacuated to a pressure of 10^{-6} Torr. The system was then closed to the vacuum pumps and the sample subjected to a programmed temperature increase. Due to the size of the leak valve chosen the amount of gas escaping into the MS analyser was insignificant and the total quantity of gas within the system rose to give a predetermined pressure of up to 20 Torr. This system was later developed [47] to include an oil diffusion pump between the vacuum microbalance and the expansion bulb. Thus, during the course of an experiment the balance was maintained at 10^{-6} Torr vacuum whilst the pressure within the bulb rose. The bulb was occasionally evacuated to maintain a working back pressure for the diffusion pump. These systems were used for desorption studies on graphite and although very suitable for this purpose their use in thermal decomposition studies is limited by the following factors.

Firstly, many reactions have been shown to be pressure sensitive and indeed the "constant rate" method of kinetic analysis relies on this fact. Secondly, the use of a diffusion pump depends on the non-interaction of the evolved gases being studied with the diffusion pump liquid and the stability of the gases at the operating temperatures of the pump. The latter is a severe limitation on a system incorporating a diffusion pump but the former depends on the pressure rise allowed and the system to be studied. All of the systems developed [45–47] were used for quantitative kinetic studies. It was found that the technique allowed measurements to be made using both the TG and EGA systems, these having been shown to be in good agreement using test reactions.

THEORETICAL CONSIDERATIONS FOR KINETIC STUDIES

It is clear from the above discussion that, although there are two main ways of analysing gases evolving from a solid, there are many variations on these methods. These are summarised in Fig. 1 which shows six such systems in a schematic form. As discussed earlier Schulman and Lochte [15] have shown how to obtain quantitative results from systems of types 4 and 5 (Fig. 1). They assumed that certain flow characteristics were maintained within those systems, this being justifiable given the high vacuum present. However, with all the other systems the gas flow characteristics must be quantified.

Inghram and Heyden [48] listed four conditions for the ideal operation of a sample introduction system. These are: (a) the composition of the gas mixture in the ionisation region should be identical with that of the sample;

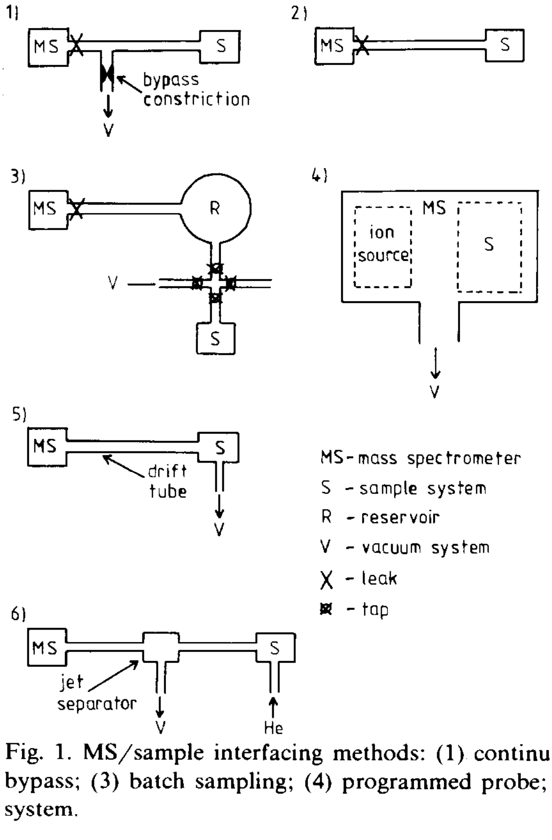

Fig. 1. MS/sample interfacing methods: (1) continuous inlet with bypass; (2) leak without bypass; (3) batch sampling; (4) programmed probe; (5) drift tube system; (6) jet separator system.

(b) the composition should not change with time as a result of the introduction system; (c) the partial pressure of each component should be independent of other components present; and (d) the gas flow rate should remain constant during the analysis. However, these requirements cannot be met entirely in any single introduction system, and an understanding of the flow conditions present in a system is necessary to avoid any serious errors in quantitative measurements.

Gas flow in any vacuum system can be any one of three types: molecular, viscous or turbulent. The last of these three, namely turbulent flow, is unlikely to be found in any MS based system and will not be discussed further. Of the other two types molecular flow prevails when the mean free path of the molecules is so large with respect to the diameter of the enclosure that intermolecular collisions can be disregarded and only collisions with the walls of the vessels are responsible for the flow resistance. Knudsen [49], showed that a practical criterion, which is now generally accepted [50], is that for free molecular flow the diameter, d, of the orifice must be not more than 1/10th of the mean free path L of the gas at the higher pressure. At $L = 2d$ the error amounts to a few percent. The factor of ten is an empirical one which offers a large margin for error. The flow rate is thus solely proportional to the partial pressure of each gas in the sample reservoir. Viscous flow by comparison, prevails when the mean free path of the molecules is small compared to the diameter of the enclosure and so, intermolecular collisions are more important than collisions with the walls. The flow rate under such conditions is proportional to the square of the total pressure of the gas mixture. Either type of flow will allow quantitative results to be obtained but combinations of both are unquantifiable. In general molecular flow is more likely to prevail at low pressures and so, since thermal decomposition reactions will begin at zero evolved gas pressure, this will now be considered.

There are three important consequences of molecular flow conditions which must be considered in the analysis of mixtures [51]. Firstly, the flow of gas out of the reservoir into the MS analyser is such that the pressure in the reservoir falls off exponentially with time. Secondly, the ratio of the partial pressures within the MS is always the same as that in the inlet reservoir. Thirdly, the lighter gases leak more rapidly from the reservoir than the heavier ones.

The quantity of gas, Q, striking an area, A, per unit time is given by

$$Q = PV = AP(kT/2\pi M)^{1/2} \tag{1}$$

where P is the pressure, V is the volume, T is the temperature, k is a constant dependent on the geometry of the system, and M is the molecular mass. When molecular flow prevails the net flow of gas across the aperture is determined by the pressure difference $P_1 - P_2$, where in this case subscript 1 refers to the sample system and 2 to the MS analyser. Changing from Q to conductance, C, to take into account this pressure difference where $C = Q/(P_1 - P_2)$ then

$$C = A(kT/2\pi M)^{1/2} \tag{2}$$

or, where $P_1 \gg P_2$ then

$$C = Q/P_1 = Sp \tag{3}$$

where Sp is the pumping speed of a system. Equation (4) shows that the flow of gas through a constriction varies inversely with square root of the molecular mass of the gas in question. The overall pumping speed of a system is determined by the combined speeds of the pumps ($Sp = S_1 + S_1 + S_3 \cdots Sn$ where n is the number of pumps within the system) and the combined conductances, C_{total}, of all components using the equation

$$\frac{1}{S} = \frac{1}{Sp} + \frac{1}{C_{\text{total}}} \tag{4}$$

This relationship is utilised in calculations involving differential pumping, i.e., the maintaining of a pressure differential between two regions inside a vacuum system by the use of apertures of low conductance between the different regions.

CONCLUSION

It is apparent from any review of MS–EGA studies that the technique is used predominantly in a qualitative manner. Thus, it has enabled reaction intermediates and products to be identified and mechanisms to be determined. However, the technique can be used in a quantitative manner, as has been discussed by a number of workers. Unfortunately the literature contains many examples of MS–EGA studies which have used systems originally designed for qualitative work to determine kinetic parameters. This is often done without the provision of adequate proof that such systems are capable of providing such quantitative results. Any system which involves less than instantaneous flow of gases from the sample to the analyser should have that flow characterised. In addition interactions between evolved gases must be understood and, if possible, the system should be calibrated for those gases.

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