*Thermochimica Acta*, 50 (1981) 49—56
Elsevier Scientific Publishing Company, Amsterdam — in The Netherlands

# A UNIVERSAL INTERFACE FOR COUPLING MASS SPECTROMETRY TO THERMOGRAVIMETRY

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(Received 12 December 1980)

## ABSTRACT

Techniques for coupling mass spectrometry (MS) to thermogravimetry (TG) have been previously described. A total condensation method is best suited for identification of off-gases at various weight loss steps. For continuous monitoring of evolved components during the weight loss process, a glass-tee interface has been found effective in most applications. The present paper describes a glass tubing-tee interface used in conjunction with a sampler to provide great versatility. Both enrichment and recovery are improved without mass discrimination. The thermogravimetric analyzer can be operated under vacuum or with a gas flow. Examples will be given to illustrate the use of this technique for either qualitative or quantitative analysis of a variety of materials.

## INTRODUCTION

Various approaches have been reported in the literature to combine the two powerful techniques, thermogravimetry (TG) and mass spectrometry (MS), for the characterization of materials. Direct connection of the TG and MS instruments is possible, but the TG experiment can be performed only under high vacuum [1—4] or under certain types of reagent gas to allow chemical ionization MS [5]. For flexible control of the atmosphere and easy adaptation to various types of instrumentation, an interface is inevitably employed. Successful interfaces reported include: metering valve [6,7], capillary [8—12], orifice [11,13,14], capillary—orifice [13,14], jet separator—orifice (15), and metering valve—jet separator [16]. However, none of these interfaces meets all the desirable features for such a coupling: easy adaptation, flexible atmosphere control, high yield, high enrichment, low mass discrimination, short time of sample transfer, and quantitative introduction of sample.

In a previous presentation, two techniques for coupling TG and MS have been described [17]. A total condensation method ensures the highest yield and enrichment with very little mass discrimination, thus ideally suited for identification of off-gases at a certain weight loss step. But this method does not monitor the off-gases along the TG profile continuously with MS. For continuous ion monitoring during the weight loss process, a glass-tee interface has been found effective. The present paper describes improved interfaces to provide great versatility. Both enrichment and yield are enhanced without much mass discrimination. The TG instrument can be operated either under vacuum or with a gas flow. Reproducible sampling is also achieved for quantitative analysis.

## EXPERIMENTAL

The schematic diagrams of the two interfaces used in this work are shown in Figs. 1 and 2. Both consist of a tee section and a constant volume sampler. The tee contains a tubing of an inside diameter of 1—2 mm, the end of which is either open to the TG furnace (Interface I) or to the sampler (Interface II). One arm of the tee is connected to the furnace tube of the duPont 951 TGA, while the other is welded to the stopcock of the sampler. The third arm is either vented into the atmosphere or connected to a duo-seal oil pump. Although the tubing-tee structure and the sampler can be made from metal, they are constructed from glass for the present work. For easy cleaning by heating, the tubing-tee part is best made from quartz. The sampler is connected to the heated inlet of the duPont 21-104 mass spectrometer. A 3-l gas reservoir and a gold leak tube are placed between the inlet and the ion source. To achieve the highest sensitivity, the sampler can also be directly connected to the ion source through a direct probe attachment.

When the TGA is operated in a flowing gas mode, the gas flows through the tubing-tee interface and vented into the atmosphere through the third arm. To take a sample for MS analysis, the sampler already under vacuum sucks in a constant volume of ca. 4 ml of gas through the tubing as soon as its stopcocks are turned momentarily. No enrichment is accomplished in this mode of operation. To enrich the sample components in a helium stream, the third arm is connected to the oil pump and both stopcocks of the sampler are open to the MS. Accordingly the mass spectra are taken continuously. Our tests with hydrocarbon mixtures show an enrichment of five times is obtainable with Interface II and two times with Interface I.

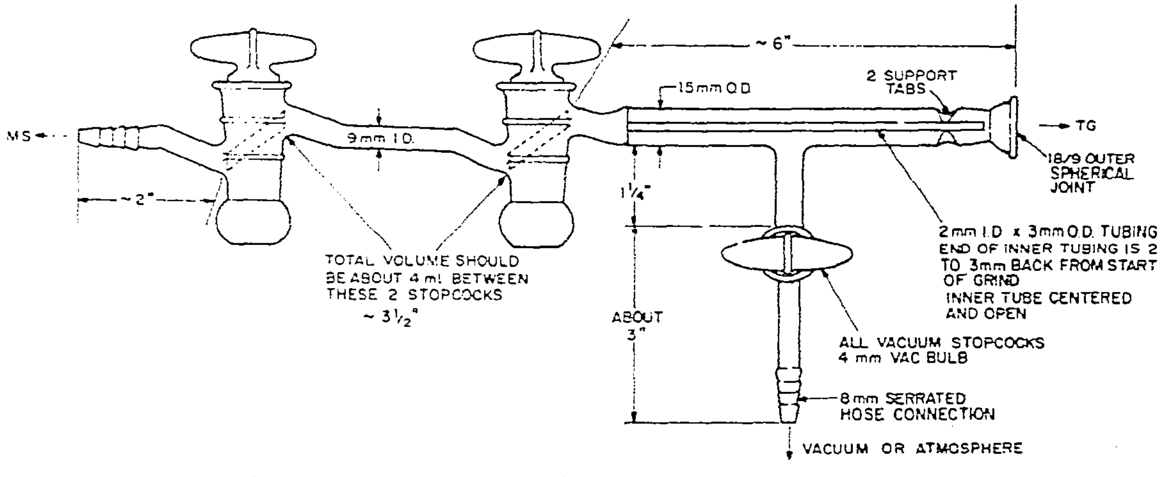

Fig. 1. Schematic diagram of TG—MS Interface I.

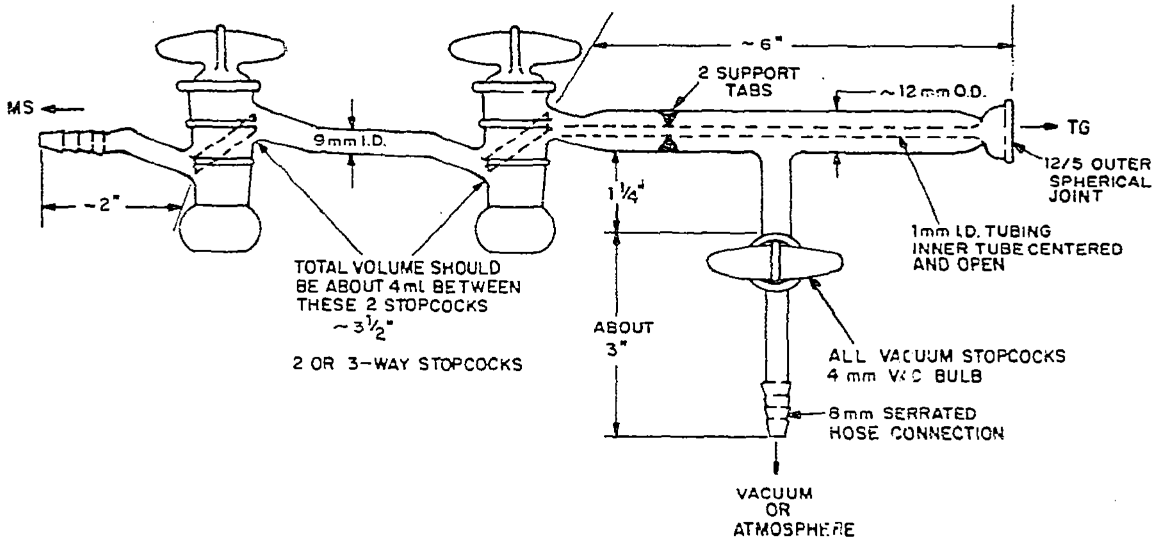

Fig. 2. Schematic diagram of TG—MS Interface II.

## RESULTS AND DISCUSSION

One of the most useful applications of coupled TG—MS is compositional analysis of unknown complex materials. For example, an aerosol spray used for coating cooking utensils was examined. After the solvent was removed, the residue was analyzed by coupled TG—MS with Interface I. As

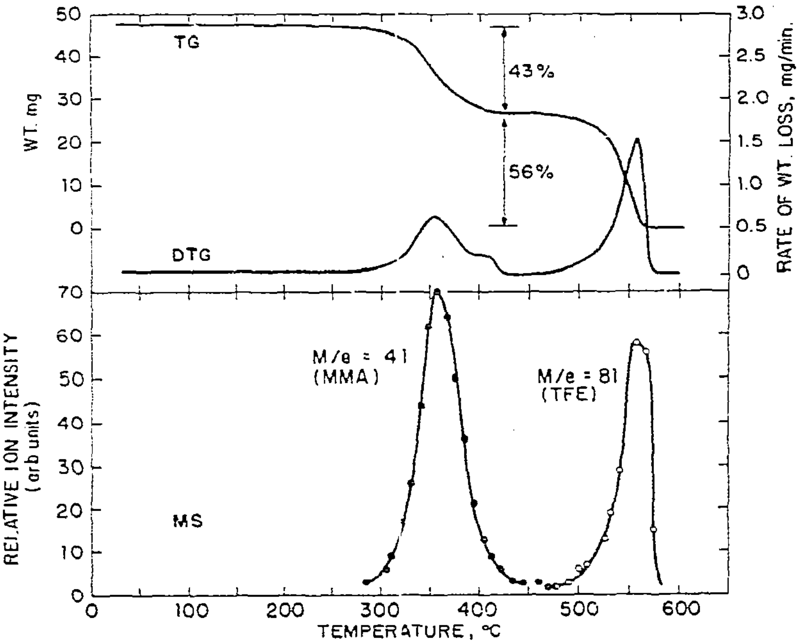

Fig. 3. TG—MS of a coating spray. Sample weight, 47 mg; heating rate, 2°C $min^{-1}$; helium flow, 30 ml $min^{-1}$; Interface I.

shown in Fig. 3, TG showed two main weight losses of 43% and 56% in the temperature ranges of 275—425°C and 475—575°C, respectively. MS identified the first weight loss as due to methyl methacrylate (MMA) and the second weight loss due to tetrafluoroethylene (TFE). If the relative ion intensities of mass peaks 41 and 81 are plotted as a function of temperature, the changes in concentrations of MMA and TFE in the volatilized products are obtained in relation to the weight loss profiles. Figure 3 shows excellent correspondence between TG and MS results. The coating is thus determined to contain 43% PMMA and 56% PTFE.

TG provides quantitative information on total weight loss at a certain temperature, but not the nature of the lost material or the amount of a specific component in the lost material. MS adds an additional capability of identification and determination of the relative composition of the off-gases. However, to relate the amount of any specific component in the off-gases to the original sample requires the determination of the absolute weight of the component from MS data. We have attempted to achieve this by introducing the sample reproducibly into the MS by means of a constant volume sampler. The technique is demonstrated by analysis of ethylene/vinyl acetate (E/VAc) copolymers. A typical weight loss curve of polyvinyl acetate or E/VAc copolymer is shown in Fig. 4. The first major weight loss step in the vicinity of 250°C involves the quantitative liberation of acetic acid, and has been used for determination of VAc content in such copolymer systems [18].

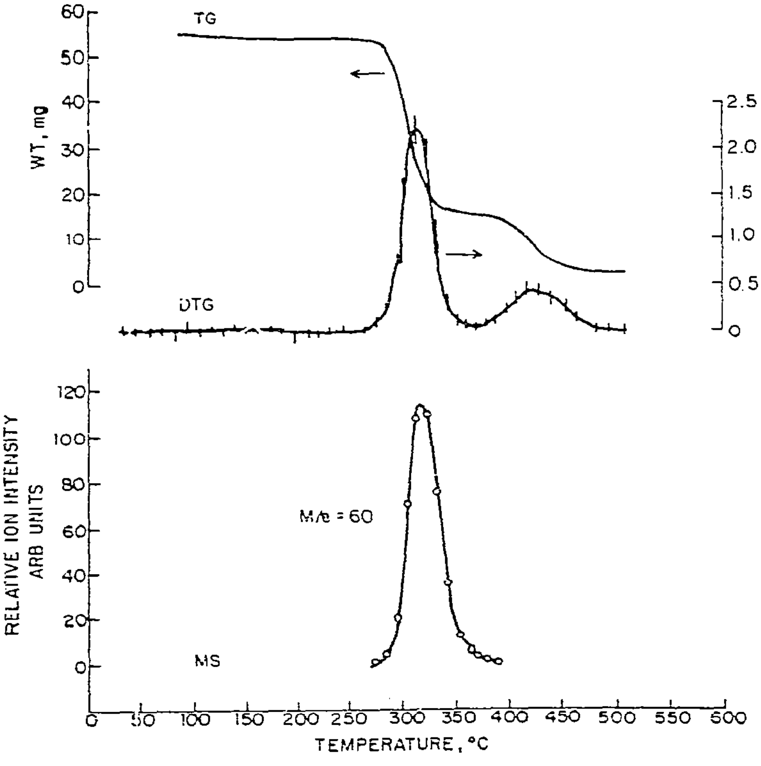

Fig. 4. TG—MS of polyvinyl acetate. Sample weight, 55 mg; heating rate, 2°C min$^{-1}$; helium flow, 30 ml min$^{-1}$; Interface I.

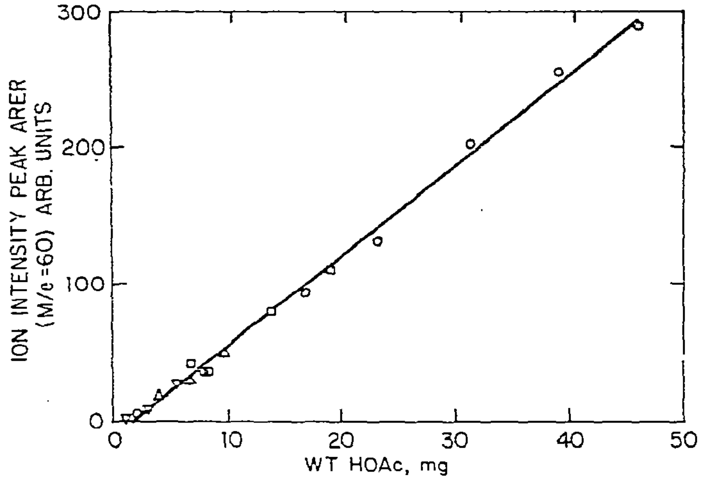

Fig. 5. Correlation of ion intensity peak area with weight of acetic acid produced from decomposition of ethylene/vinyl acetate copolymers. (○) 100% VAc; (□) 39.1% VAc; (△) 19.9% VAc; (▽) 8.8% VAc.

When the relative ion intensity of mass peak 60 of acetic acid is plotted vs. temperature, as shown in Fig. 4, the integrated peak area is a measure of the total amount of acetic acid. This is shown in Fig. 5 by plotting the peak area vs. the weight of acetic acid for four polymer standards containing 8.8, 19.9, 39.1 and 100% VAc, respectively. The correlation is quite satisfactory. Such a technique is very useful in the determination of a selected component without interference from other materials.

One main feature of the present interface is its flexibility to allow atmosphere control. This is illustrated in the degradation of calcium acetate monohydrate in various atmospheres as studied by the TG—MS technique using Interface II. In a flowing helium atmosphere, calcium acetate monohydrate shows three main stages of weight loss: stepwise dehydration, decomposition of the acetate to form acetone and calcium carbonate, and decarboxylation to generate carbon dioxide. These products are clearly shown in the mass spectral data at various weight loss steps shown in Fig. 6. The degradation mechanism for the second weight loss step is completely different in an oxidative atmosphere, as shown in Fig. 7. Violent combustion results in rapid evolution of carbon dioxide and water, and very little acetone is produced. The results obtained under vacuum are similar to those obtained in an inert atmosphere as expected, and shown in Fig. 8. It should be noted that the ion intensities are much more intense in the vacuum runs mainly because of sample enrichment through the use of the interface.

The high resolution of the present instrumentation has revealed the complex nature of the seemingly simple decomposition of calcium acetate monohydrate. The existence of two intermediate hydrates, $Ca(CH_3COO)_2 \cdot 0.5\ H_2O$ and $Ca(CH_3COC)_2 \cdot 0.25\ H_2O$, are confirmed by both TG and MS results shown in Figs. 6—8 [19]. The decomposition of the acetate to produce acetone apparently also involves other side reactions.

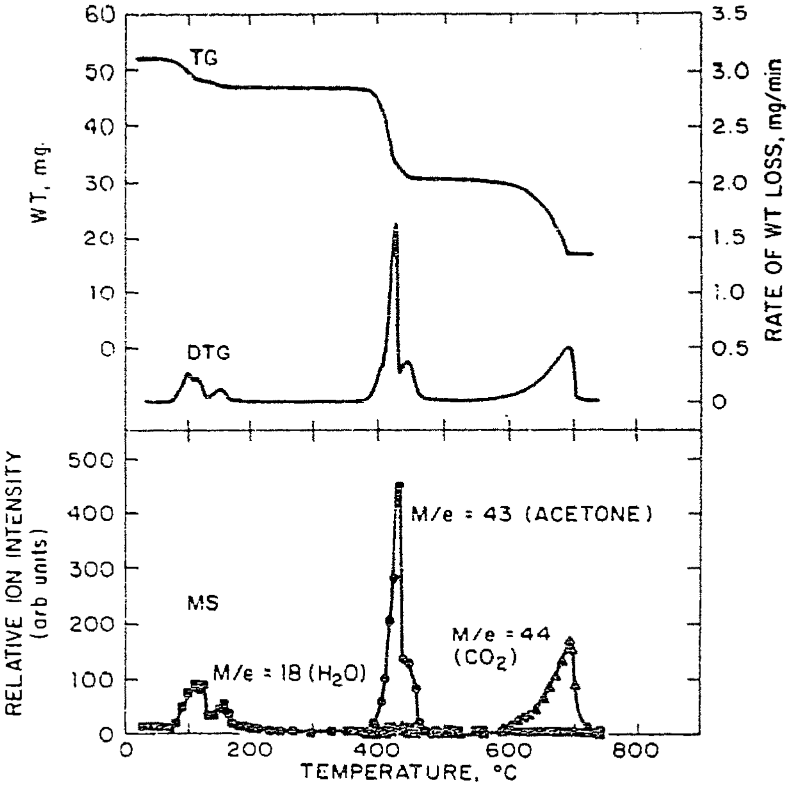

Fig. 6. TG—MS of calcium acetate monohydrate. Sample weight, 52 mg; heating rate, 2°C min$^{-1}$; helium flow, 30 ml min$^{-1}$; Interface II.

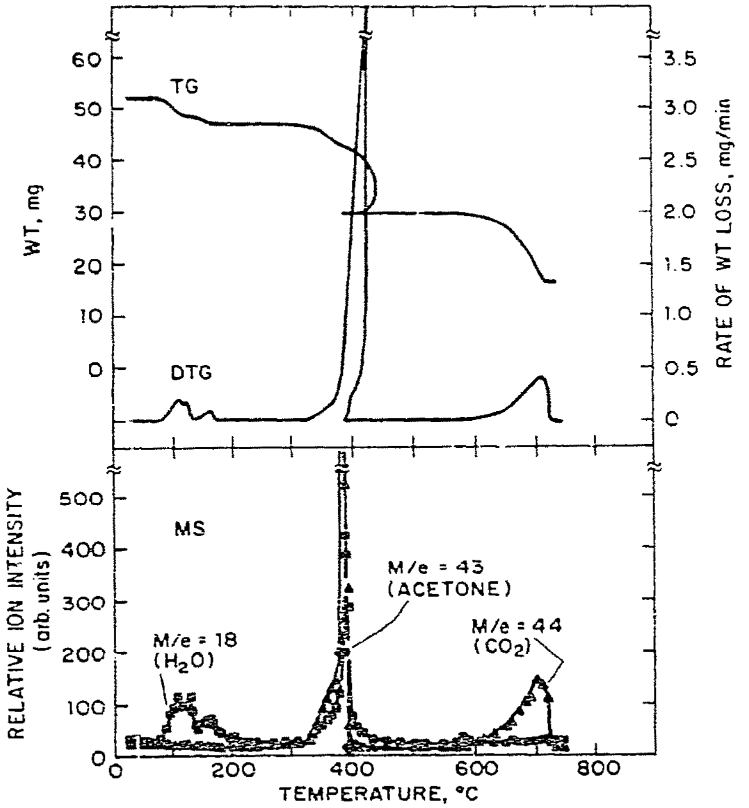

Fig. 7. TG—MS of calcium acetate monohydrate. Sample weight, 52 mg; heating rate, 2°C min$^{-1}$; air flow, 30 ml min$^{-1}$; Interface II.

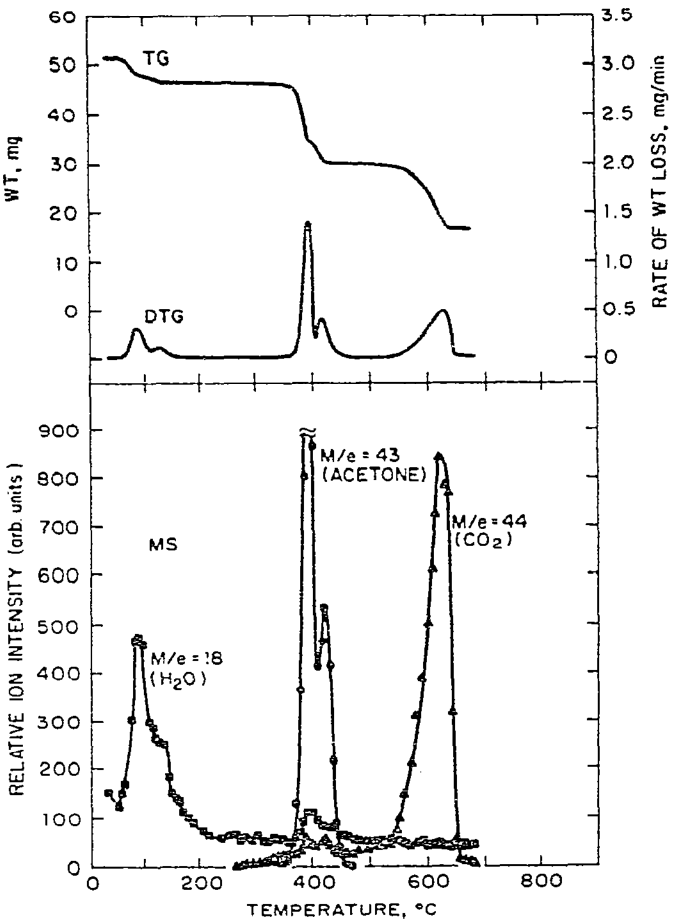

Fig. 8. TG—MS of calcium acetate monohydrate. Sample weight, 52 mg; heating rate, 2°C min$^{-1}$; vacuum, 10 Torr helium; Interface II.

## CONCLUSION

A unique interface for coupling TG and MS has been described, which can be readily adapted to most existing instruments, allows atmosphere control, and provides reproducible sample introduction for quantitative analysis. The interface has the potential of further automation through the use of electronic devices. Many important applications can be visualized. For instance, kinetic studies of overlapping reactions are possible through selective ion monitoring during the weight loss measurements.

## ACKNOWLEDGEMENT

The authors wish to thank R.A. Parkinson for his skillful experimental assistance and many helpful discussions.

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