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TECHNIQUES FOR COUPLING MASS SPECTROMETRY TO THERMOGRAVIMETRY

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ABSTRACT

Techniques combining thermogravimetry (TG) and mass spectrometry (MS) are described whereby TG provides precise heating conditions and weight loss information and MS identifies volatiles evolved during the weight loss process. In the present work the DuPont 990 thermal analysis system, a DuPont 21-104 mass spectrometer, and a Hewlett-Packard 21-MX/Digital Equipment PDP-10 computer system are combined through simple, unique interfaces. The instrumentation features flexibility in thermal treatment of the sample and good atmospheric control. Tests with model substances and practical industrial problems have shown good enrichment and recovery of eluted components and no significant delay in TG operations.

INTRODUCTION

Thermogravimetry (TG) coupled to mass spectrometry (MS) constitutes a very powerful technique for materials characterization. The former provides precise heating conditions and weight loss information, whereas the latter identifies volatiles evolved during the weight loss process. Many attempts have been made to achieve this combination during the past decade. The main emphasis of research efforts has been centered around the development of an interfacing system to suit the particular TG and MS instruments being used. Techniques reported include direct connection under vacuum [1—5], direct connection under reagent gas [6], the use of metering valves [7,8], and the use of capillary-orifice [9—13]. It appears to be a rather difficult task to develop an interface to meet the requirements of an ideally coupled TG—MS system such as free choice of vacuum or atmospheric pressures, no dilution of the sample of interest, no mass discrimination, no loss of highly volatile or non-volatile components, continuous monitoring, and easy adaptation to various instruments. The present paper describes two simple coupling techniques which meet most of the requirements. Even though the DuPont Model 951 TG and the DuPont Model 21-104 MS instruments were used to test the coupling system, other equivalent apparatus should be readily adaptable.

EXPERIMENTAL

A schematic diagram of the coupled TG—MS system is shown in Fig. 1. In the first technique, the interface used is a six-port microvalve (Cat. No. 5521, Carle Instruments, Fullerton, CA) connected to a U-shaped liquid nitrogen trap made of ca. 3 in. × 1/16 in. outer diameter stainless steel or glass tubing. A liquid nitrogen protection trap is added on the exhaust side to prevent back-diffusion of room air. The quartz furnace tube of the TG apparatus has been modified with the spherical joint replaced by a short piece of 1/8 in. outer diameter quartz tubing which fits into the 1/8 in. end of a Swagelok® reducing union (Part No. SS-200-6-1). The 1/16 in. end of the union is connected to the microvalve. The 1/8 in. nut is tightened to the union with the front ferrule removed and the back ferrule reversed against a O-ring (Viton®) to make the seal. A conditioner maintained at a pre-selected temperature may be added after the furnace tube to remove undesirable less volatile materials to prevent clogging of the microvalve and contamination of the MS. The organic vapors evolved during a certain weight loss step are completely condensed in the liquid nitrogen trap and then evaporated into the MS by properly switching the microvalve. No dilution of the sample results when helium is used as the carrier gas. It is desirable to add a metering valve between the TG apparatus and the helium source to obtain better control of the flow. A Model 21-MX computer (Hewlett Packard, Cupertino, CA) is used to compute the MS data. This technique is highly sensitive to determine trace amounts of effluents from TG, and provides both qualitative and quantitative analyses of the off-gases during a weight loss step. However, it is not suitable for continuous monitoring during the weight change process.

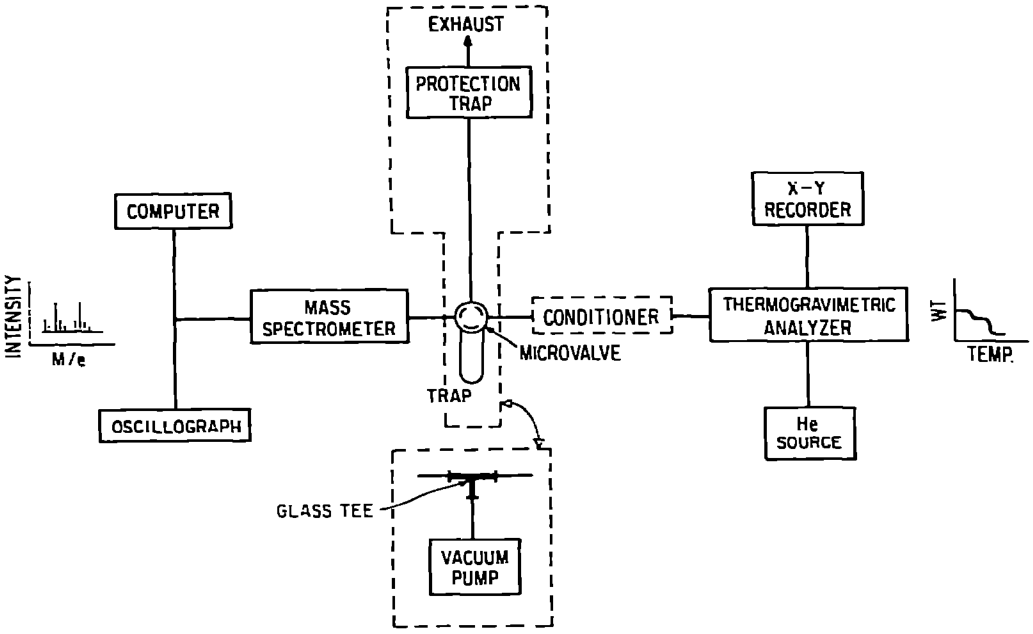


Fig. 1. Schematic diagram of TG—MS system.

The second technique replaces the microvalve-trap system along with the protection trap by a regular glass tee as shown in the dashed portion of Fig. 1. To connect the quartz tubing end of the TG furnace tube to the 10-mm outer diameter glass tee, a 1/8—1/4 in. Swagelok® union (Part No. SS-400-6-2) is used with the 1/4 in. side connected to a 1-in. length of stainless steel tubing which in turn is attached to the glass tee through butyl rubber tubing. Another arm of the tee is connected to the heated inlet system of the MS through butyl rubber tubing. The third arm of the tee is connected to a Model 1402 duo seal oil pump (Welch Scientific Co., Skokie, IL). By properly controlling the carrier gas flow and the sample size, most organic vapors of interest are led into the MS. Thus, the differential pumping capability between this pump and the MS pump functions to sample the heavier molecules from the helium stream with some enrichment.

RESULTS AND DISCUSSION

Total condensation method

The TG is operated by the normal procedure. A sample size in the mg range is used, dependent on the total volatiles evolved. A heating rate of 10°C min^{-1} or lower is preferred for good resolution of thermal events, although a higher rate can be used for rapid analysis. The derivative TG (DTG) curve is used to better define the weight loss step, while the TG curve provides more convenient calculation of the absolute weight.

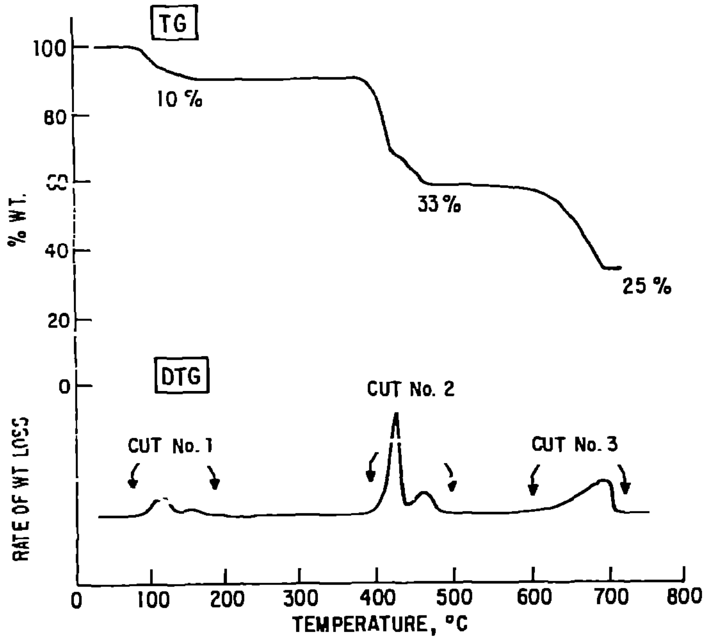


Fig. 2. TG of calcium acetate monohydrate. Sample weight, 11 mg; heating rate, 10°C min^{-1}; helium flow, 60 ml min^{-1}; sensitivity, 2.0 mg in.$^{-1}$ on Y and 1.0 mg min^{-1} in.$^{-1}$ on dY.

Figure 2 shows the TG and DTG scans of a reagent-grade calcium acetate monohydrate. Volatiles evolved during the three distinct weight loss steps are condensed consecutively in the liquid nitrogen trap without interrupting the TG scan. The trap is then warmed and the trapped gases injected into the MS for identification. The corresponding MS spectra are shown in bar graphs in Fig. 3a, b and c for cuts 1, 2, and 3, respectively. The main components identified as water, acetone, and carbon dioxide in cuts 1, 2, and 3, respectively, are consistent with the following reactions well established for decomposition of calcium acetate monohydrate. The quantitative information ob-

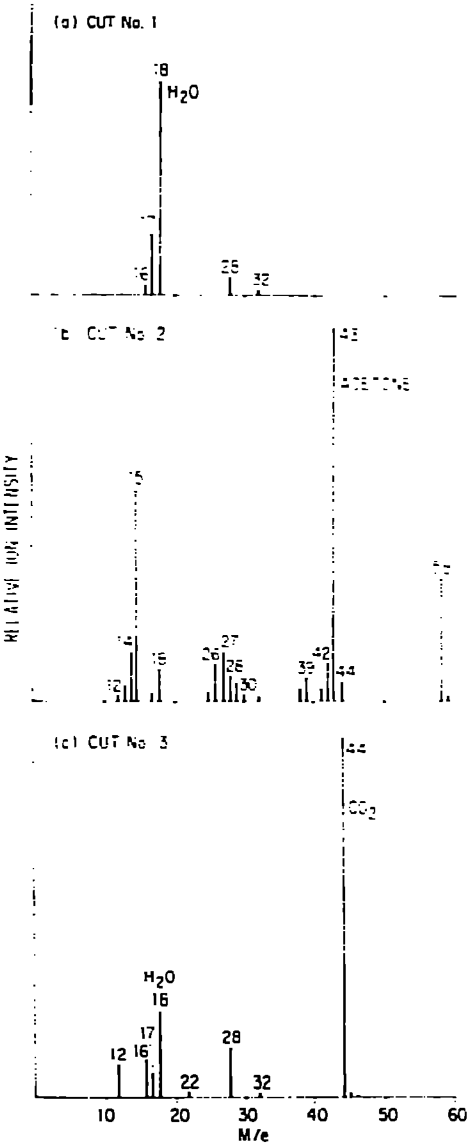


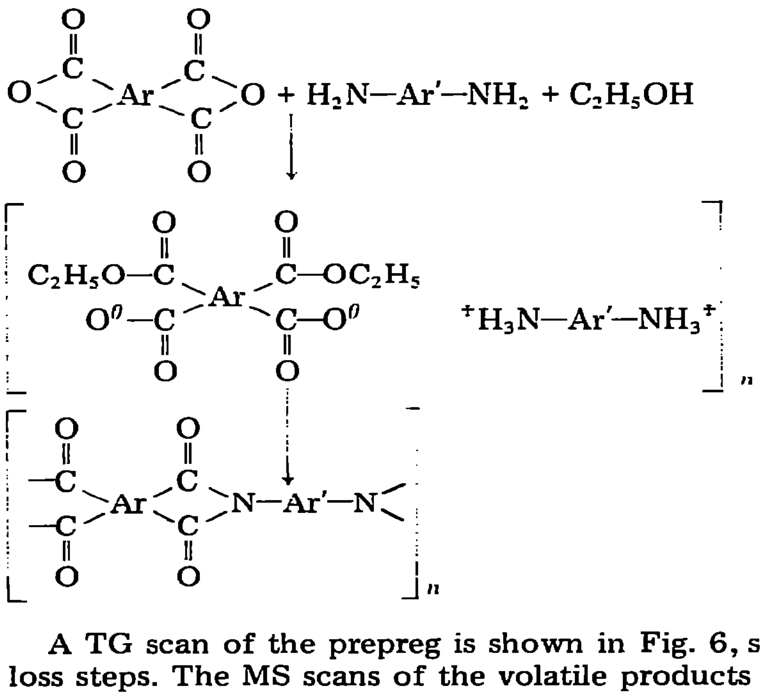
Fig. 3. MS spectra of volatile products from TG of calcium acetate monohydrate. (a), (b) and (c) are for weight loss cuts 1, 2 and 3 shown on the DTG curve.

tained from the TG scan also agrees with the stoichiometric values as expected.

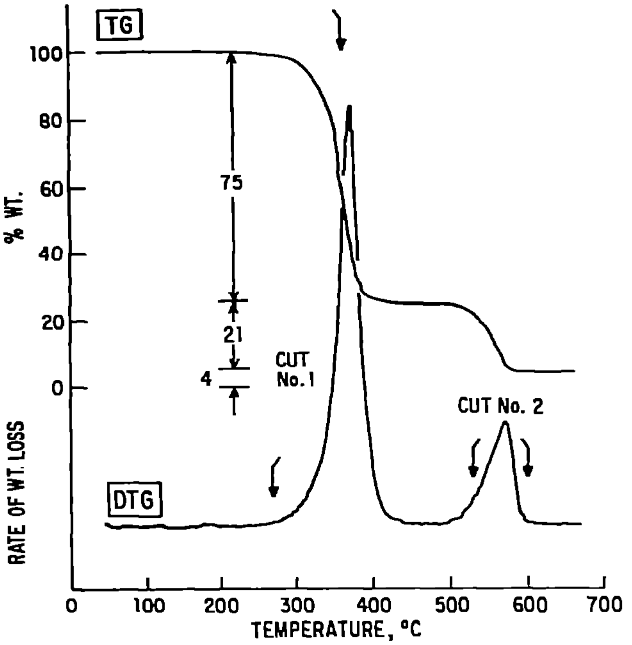
$Ca(OCOCH_3)_2 \cdot H_2O$
↓
$Ca(OCOCH_3)_2 + H_2O$ (10.2%)
↓
$CaCO_3 + CH_3COCH_3$ (33.0%)
↓
$CaO + CO_2$ (25.0%)

In another example a polyacetal resin part was analyzed by the TG—MS technique. TG showed clearly two weight loss steps involving 75 and 21%, respectively (Fig. 4). MS analyses of the two cuts corresponding to the two weight loss steps showed mainly formaldehyde for the first cut and tetrafluoroethylene for the second cut (Fig. 5a and b). Since polyoxymethylene (POM) and polytetrafluoroethylene (PTFE) are known to depolymerize almost completely into their respective monomers, the resin part probably consists of 75% POM and 21% PTFE by weight.

The technique has been effectively used to study the curing of an experimental polyimide prepreg prepared by heating for a few minutes at 120°C a binder solution in ethanol applied to graphite roving. Presumably after heating the binder is in a diester—diammonium salt form, and further curing of the composition will eliminate water and ethanol to form the polyimide.



A TG scan of the prepreg is shown in Fig. 6, showing three major weight loss steps. The MS scans of the volatile products evolved during these steps are shown in Fig. 7a, b and c. Evidently, elimination of water and ethanol is involved in all three steps, contrary to the prior assumption that dehydration of the ammonium salt to form amide would be followed by elimination of ethanol to form the imide. Also, the detection of water and ethanol at temperatures as high as 300°C indicates complete curing only at high temperatures.



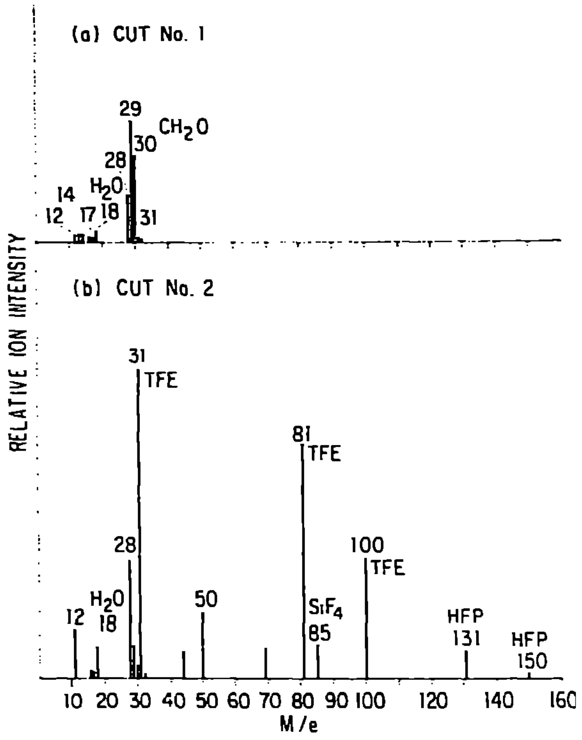


Fig. 4. TG of a resin part. Sample weight, 6 mg: heating rate, 10°C min^{-1}; helium flow, 60 ml min^{-1}; sensitivity, 1.0 mg in.$^{-1}$ on Y and 0.2 mg min^{-1} in.$^{-1}$ on dY.

Fig. 5. MS spectra of volatile products from TG of a resin part. (a) and (b) are for weight loss cuts 1 and 2 shown on the DTG curve.

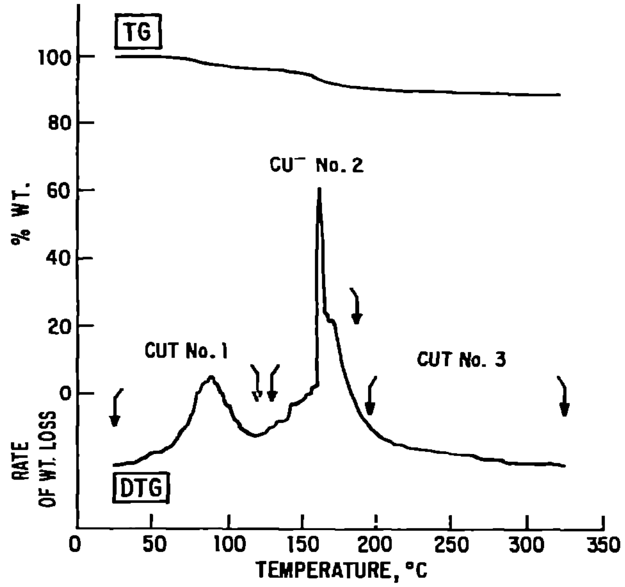
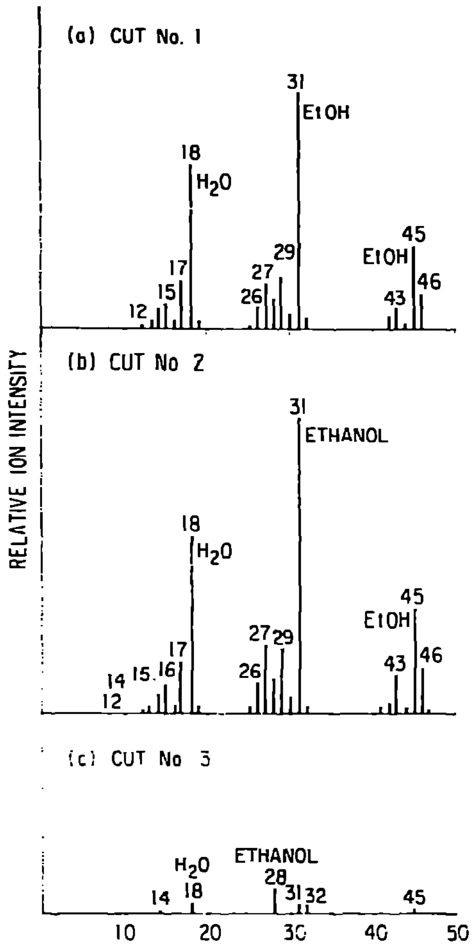


Fig. 6. TG of a polyimide prepreg. Sample weight, 25 mg; heating rate, 10°C min^{-1}; helium flow, 60 ml min^{-1}; sensitivity, 5.0 mg in.$^{-1}$ on Y and 0.2 mg min^{-1} in.$^{-1}$ on dY.



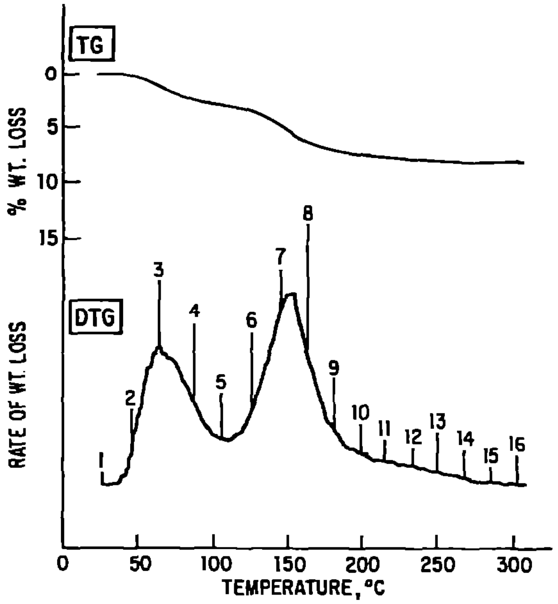


Fig. 7. MS spectra of volatile products from TG of a polyimide prepreg. (a), (b) and (c) are for weight loss cuts 1, 2 and 3 shown on the DTG curve.

Fig. 8. TG of polyimide prepreg with continuous monitoring by MS. Sample weight, 76 mg; heating rate, 5°C min^{-1}; helium flow, 60 ml min^{-1}; sensitivity, 5 mg in.$^{-1}$ on Y and 0.2 mg min^{-1} in.$^{-1}$ on dY.

Continuous monitoring method

By using the glass tee as the interface, MS scans can be taken continuously every 2 min. The 3-l pressure chamber in the heated inlet system of the MS is evacuated at each sampling to remove the residual volatiles of the preceding point. Thus, the MS scan follows the TG curve closely to provide interpretation of the thermal events. A heating rate of 5°C min^{-1} has been found to be quite satisfactory. Tests with a mixture of hexane and decane showed an enrichment of 3, a yield of 20%, and essentially no mass discrimination of the two compounds.

Figure 8 shows a continuous TG scan of the polyimide prepreg with MS scans taken sequentially every 2 min as numbered on the DTG curve. The two major components, water and ethanol, are monitored by mass peaks 18

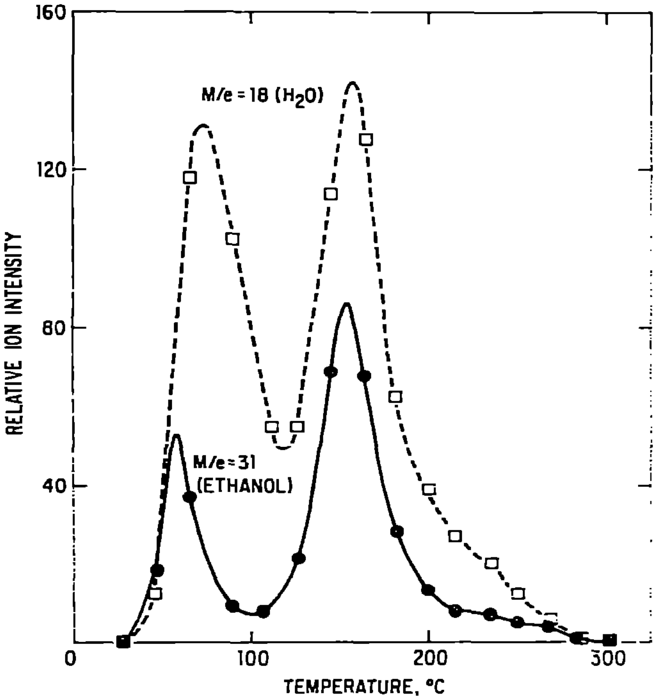


Fig. 9. Relative ion intensity plots of volatile products from TG of a polyimide prepreg as a function of temperature.

and 31, respectively, and their relative ion intensities are plotted as a function of temperature (Fig. 9). The results essentially confirm the previous conclusion that water and ethanol are involved in all weight loss steps. It is possible that the first weight loss step arises from evaporation of residual ethanol solvent after B-staging and loss of adsorbed water on graphite. The second weight loss step is ascribed to imidization producing water and ethanol almost simultaneously. Careful examination of the evolution curves indicates a fast curing step followed by a slow one. The imidization is not complete until the temperature is beyond 300°C.

CONCLUSION

Two simple techniques have been described to couple thermogravimetry to mass spectrometry to provide valuable information on composition of materials, degradation characteristics, and reaction mechanisms. The continuous monitoring method, in addition, can resolve overlapping reactions by following concentration changes of individual components, and the kinetic parameters of such overlapping reactions can be obtained by using computation techniques similar to those proposed previously [2,11].

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