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THERMOGRAVIMETRY COUPLED WITH ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETRY. A NEW COMBINED TECHNIQUE

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ABSTRACT

Although thermogravimetry has proven to be an extremely useful analytical technique, there are cases where the compositional information derived from this technique is insufficient. A combined thermogravimetric–mass spectrometric technique might be useful to analyze the effluent gases. In an ideal world, the thermogravimetric analyzer would feed directly into the mass spectrometer source. In actual practice, however, flowing gases from the thermogravimetric analyzer are incompatible with the vacuum necessary for mass spectrometer operation.

This study presents a new approach to this problem: interfacing the thermogravimetric analyzer to a mass spectrometer designed for atmospheric pressure chemical ionization (APCI). This combined system has demonstrated the ability to distinguish between groups of samples having similar thermogravimetric behavior.

INTRODUCTION

The ability of thermogravimetry to solve a great variety of analytical problems is amply documented in the literature. There are cases, however, where the compositional information derived from this technique is insufficient. Additional information may be needed to answer the analytical questions about the sample and its composition. A combined technique might then be applied, such as analyzing the effluent gases from the thermogravimetric analyzer. In an ideal world, the thermogravimetric analyzer would feed directly into the source of the mass spectrometer, and as the samples changed weight due to heating, real-time analysis of the evolved gases would take place. In actual practice, however, the flowing gases from the thermogravimetric analyzer and the vacuum necessary for the operation of the mass spectrometry are incompatible. There have been several solutions

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to this problem reported in the literature. These include total vacuum systems [1–3], the use of inlet purge gases [4], micrometering valves [5], constant volume samplers [6,7], and jet separators [8,9].

This study presents a new approach to the problem: interfacing the thermogravimetric analyzer to a mass spectrometer designed for atmospheric pressure chemical ionization (APCI). The mass spectrometer used was the Sciex TAGA 3000, a quadrupole mass spectrometer, which had been developed for atmospheric trace gas monitoring and stack effluent analysis [10,11].

A complete description of how the Sciex TAGA 3000 operates is already in the literature [12]. In brief, gases flowing into the APCI source are ionized in a discharge corona and are guided by electrostatic fields through an orifice in the atmospheric pressure-to-vacuum interface while the unionized gas molecules and particulates are diverted away by a counter current flow of ultrapure nitrogen. The ions are collimated by the ion optics into the quadrupole mass filter for mass separation.

Associated with the unique design of the TAGA 3000 inlet system is the atmospheric pressure chemical ionization process. The initial ionization is electron bombardment of nitrogen. The N_2^+ ion then undergoes a charge transfer reaction with oxygen. The O_2^+ forms a cluster with water vapor in the air and by a series of reactions forms the proton hydrate, H_3O^+. This ion clusters with other water molecules to form a series of proton hydrates $H_3O^+ \cdot (H_2O)_n$. Sample molecules entering the system react with the proton hydrates. A proton or proton and water molecule is transferred to each molecule. For effective proton transfer, proton affinity of the molecule of interest must be higher than that of water. This is generally true for any organic compound containing a heteroatom such as N, O, P or S.

INSTRUMENTATION

The equipment used in this study is illustrated in Fig. 1. The Perkin-Elmer TGS-2 thermogravimetric analyzer was temperature controlled by the Per-

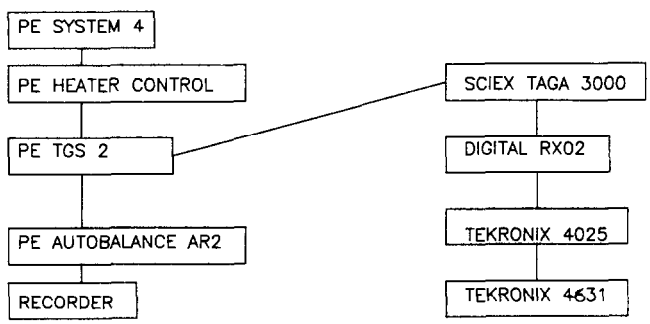

Fig. 1. Instrumentation diagram.

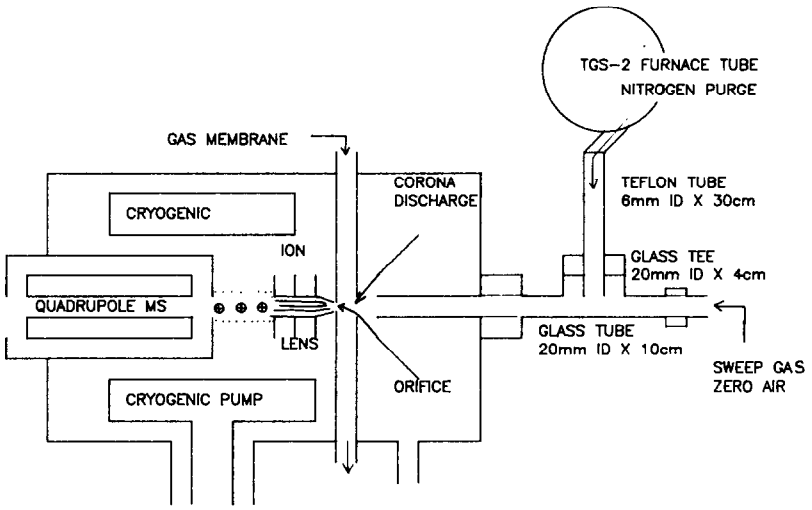

Fig. 2. The TGS-2–TAGA 3000 interface.

kin-Elmer System 4 microprocessor controller. The furnace was calibrated using the System 4 calibration routine. The output of the TGS-2 balance was recorded as percent of total sample weight on either a Fisher Recordall strip chart recorder or a Bascom Turner 8020 recorder.

The Sciex TAGA 3000 mass spectrometer system was supported by a data system consisting of a Digital RXO2, Tektronix 4025 terminal and Tektronix 4631 hard copier. The software controls the mass spectrometer's operating parameters and allows for the collection of mass scans on to floppy disks for later recall and manipulation.

The interface transfer lines from the TGS-2 to the TAGA are illustrated in

TABLE 1

Operating conditions

TGS-2
Temperature program: hold 1 min at 50°C,
heat 50–600°C at 25° min^{-1},
hold 3 min at 600°C
Purge gas: N_2 at 80 ml min^{-1}
Sample mass: 6–15 mg
Balance output: 100% sample weight full scale
TAGA 3000
Masses scanned: 15–175 a.m.u.
Ionization mode: positive
Sweep gas: zero air at 0.9 l min^{-1}
Output: 27 mass spectra at 1 min intervals

Fig. 2. This figure also provides a schematic of the sample path from the TGS-2 through the mass spectrometer. The effluent from the TGS-2 flows through a teflon transfer line (30 cm × 6 mm i.d.). Five centimeters of this tube project through a teflon O-ring inside a threaded cap into short arm of the glass tee (6 cm × 20 mm i.d.). The effluent gas encounters a flow of sweep gas (zero air) in the long tube of the tee (10 cm × 20 mm i.d.), which projects into the TAGA front end. The teflon transfer line is attached to the exit port of the furnace tube by an oversleeve of heat-shrinkable tubing, which allows a flexible joint. The length of the transfer line is minimized but still allows the necessary vertical travel of the furnace tube. The whole transfer assembly remains in place during sample loading of the balance.

Table 1 lists the operating parameters for the TGS-2 and the TAGA. The flow of ultrapure nitrogen through the balance is maintained at 80 ml min^{-1}. This flow rate minimizes the residence time of the effluent gases in the furnace tube but does not contribute to balance instability by excessive turbulence. Likewise, the flow rate of the sweep gas (zero air) through the glass tee is set at 0.9 l min^{-1}, providing sufficient sweep velocity without excessive dilution of the effluent gases. It has been hoped that the need for the sweep gas could be eliminated and the effluent from the TGS-2 could be fed directly into the TAGA. While this is possible when the balance purge gas is air, there are insufficient oxygen molecules in the nitrogen purge to maintain a stable corona discharge in the TAGA. Sample sizes of 6–15 mg for the TGS-2 were selected as a compromise between efficient balance operation and overloading the mass spectrometer.

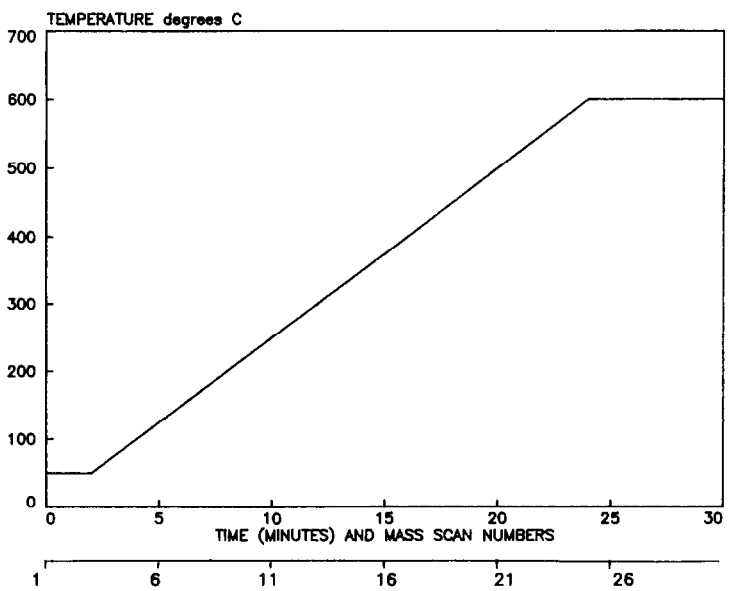

Fig. 3. Temperature and mass data collection program.

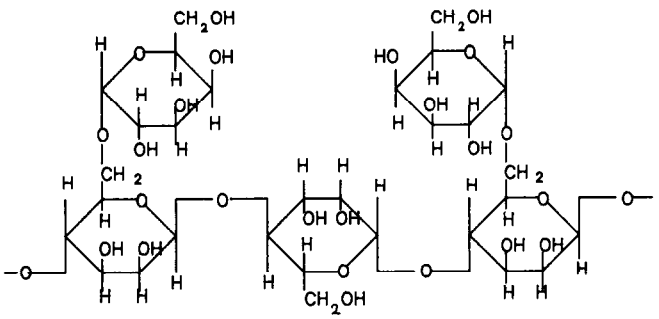

Fig. 4. Guar gum structure.

The TAGA operating parameters were set to collect mass fragments produced in the positive mode of ionization (protonation). The mass spectrometer was set to scan the mass range from 15 to 175 a.m.u. and to begin a new scan each minute. The beginning scan was coordinated with the beginning of the temperature program and a mass scan for each 25° rise in program temperature was collected. This collection rate was chosen over a faster scan rate with a narrower mass range, or faster rate with non-reproducible times between scans. It was determined that the wide mass scan range was justified for the variety of samples to be analyzed. Another data collection alternative is possible, that of monitoring the abundance of eight preselected ions with time. This would allow rapid scanning over the eight masses and produce several scans per minute. This option was not selected as the mass numbers of the test sample fragments were unknown.

The actual sample run proceeded as follows. The sample was loaded onto the TGS-2, the balance closed, the purge gas started, and the sample weighed. The temperature program illustrated in Fig. 3 was simultaneously started with the mass data collection program for the TAGA. The TGS-2 balance results were recorded as 100% sample weight full scale and the mass

TABLE 2

Guar gums used

Food grade guar	(FG)
Glyoxal guar	(G)
Hydroxyethyl guar	(HE)
Hydroxypropyl guar	(HP)
Sodium carboxyethyl guar	(SCE)
Sodium carboxymethyl guar	(SCM)
3-Trimethylamino-2-hydroxypropyl guar chloride	(TMHP)

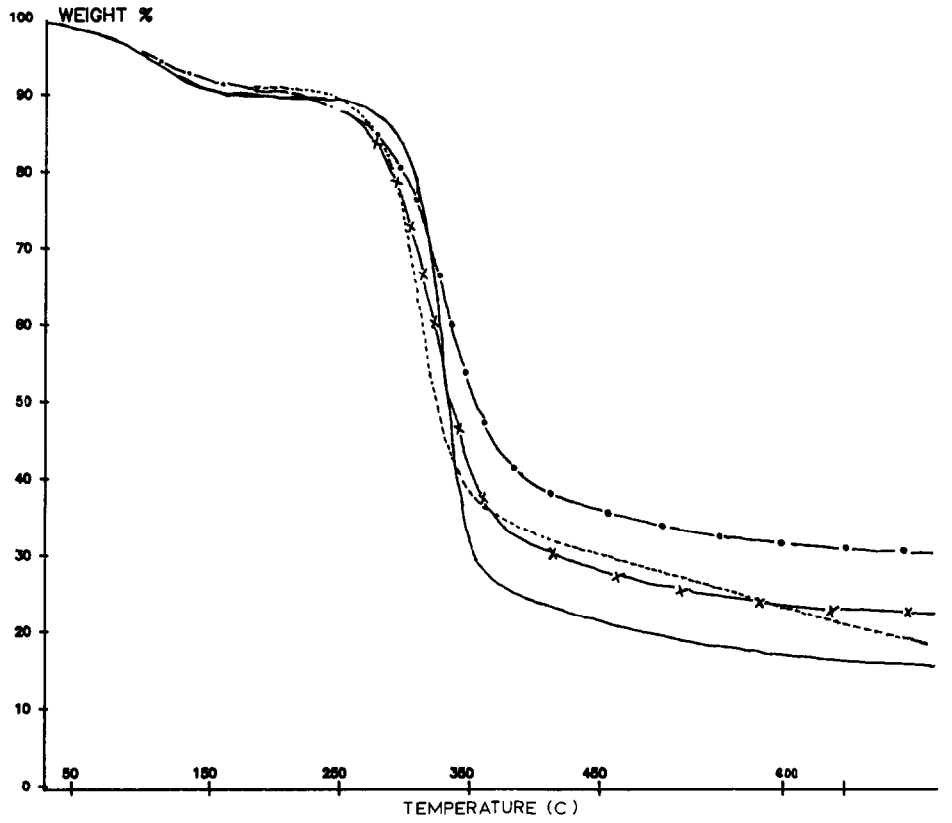

Fig. 5. Comparison of thermogravimetric curves for modified guar gums. ———, Food grade; ·–·–·, hydroxyethyl; —×—, hydroxypropyl; ·····, 3-trimethylamino-2-hydroxypropyl guar chloride.

scans were sequenced at one minute intervals, allowing a mass scan–temperature correlation.

APPLICATION OF THE COMBINED SYSTEM

A series of guar gums, in natural and chemically modified form, was used to test the utility of this combined TGS-2–TAGA system. The literature [13] reports that guar gums have been analyzed by TG–DTA. A guar gum is essentially a polysaccharide having a straight chain of D-mannopyranose units joined by a beta (1–4) linkage with a side branching unit of single D-galactopyranose joined to every other mannose unit by an alpha (1-6) linkage (Fig. 4). Table 2 lists the guar gums used in this study. Figures 5 and 6 illustrate the thermogravimetric curves of the food grade guar gum and gums which have been chemically modified. It is noted that the glyoxal-

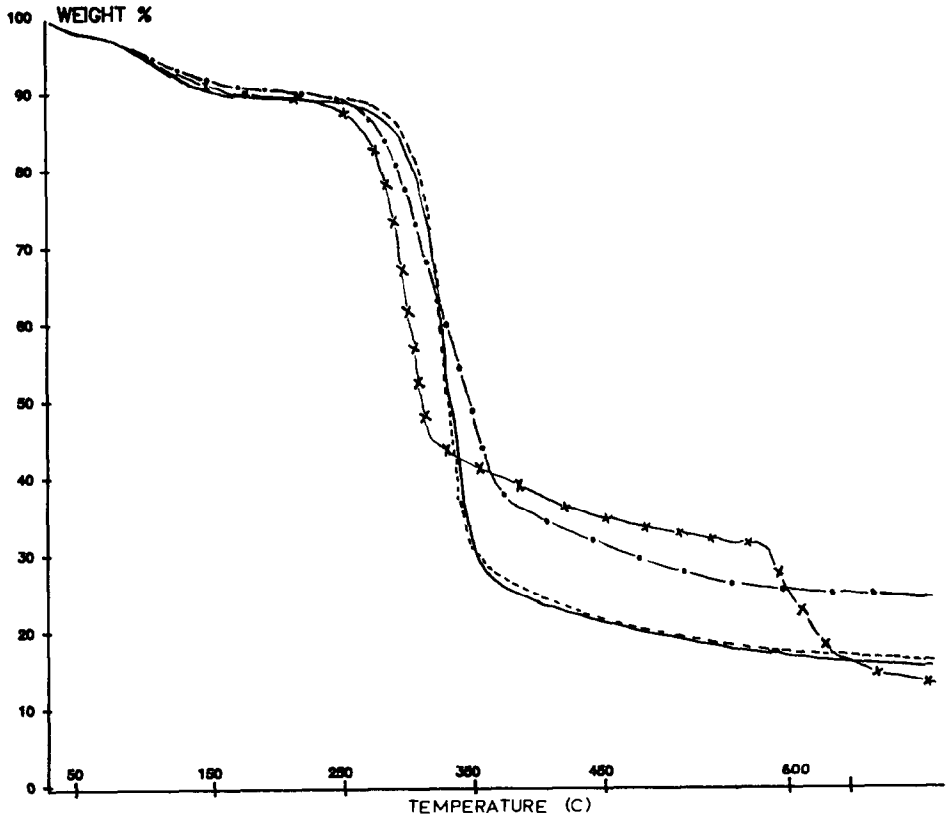

Fig. 6. Comparison of thermogravimetric curves for modified guar gums. ———, Food grade; ·–·–·, sodium carboxyethyl; —×—, sodium carboxymethyl; ·····, glyoxal.

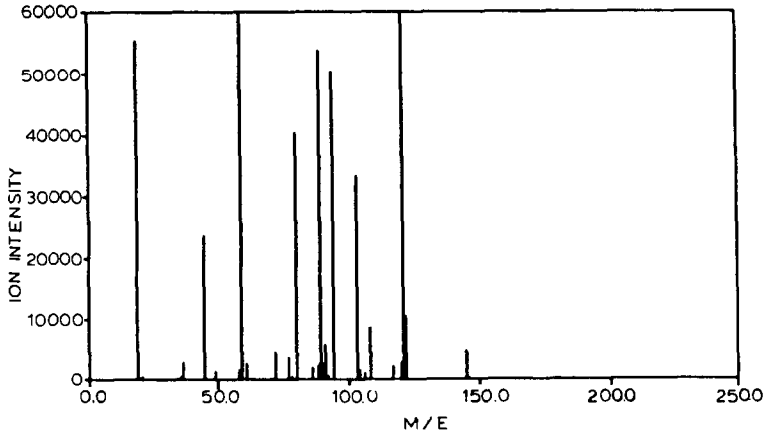

Fig. 7. Averaged mass spectrum. Hydroxyethyl guar.

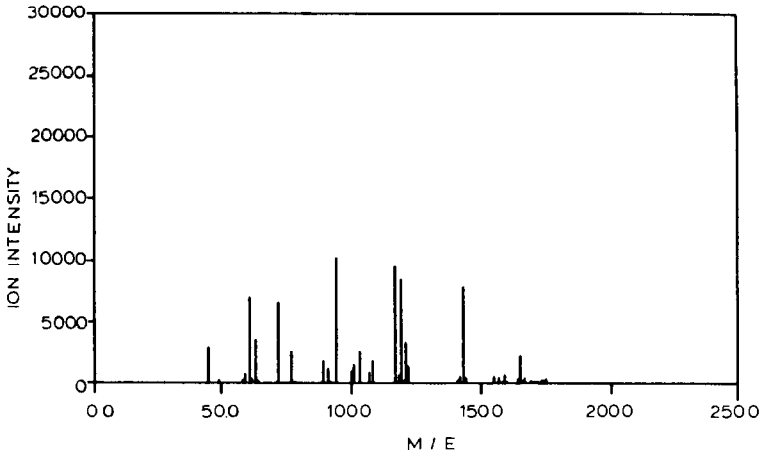

Fig. 8. Averaged mass spectrum. Hydroxypropyl guar.

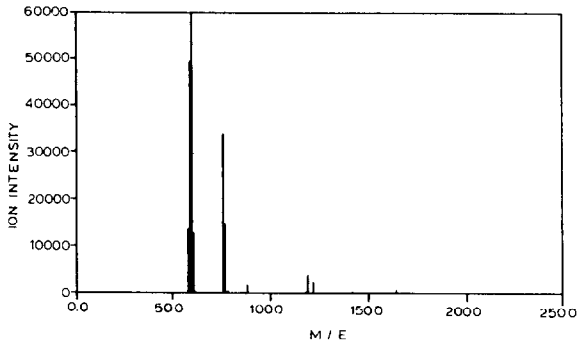

Fig. 9. Averaged mass spectrum. 3-Trimethylamino-2-hydroxypropyl guar chloride.

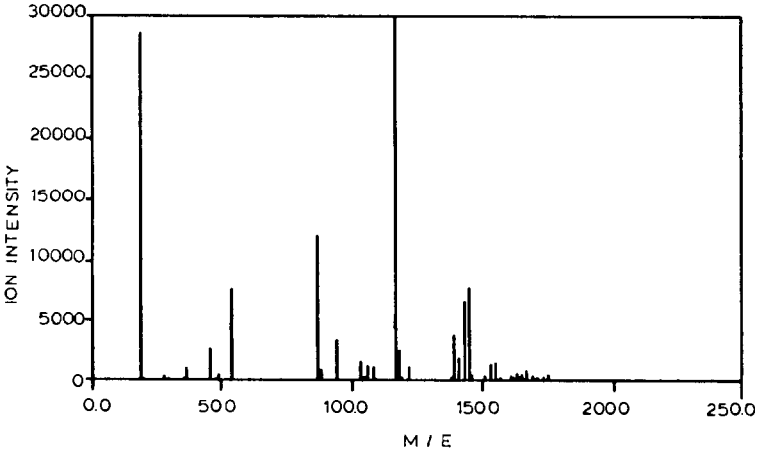

Fig. 10. Averaged mass spectrum. Sodium carboxyethyl guar.

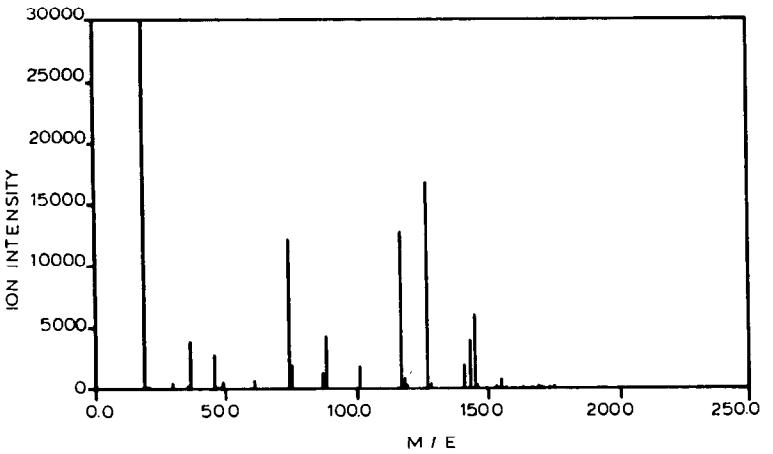

Fig. 11. Averaged mass spectrum. Sodium carboxymethyl guar.

treated guar gum is most similar to the unmodified gum and, on the basis of thermogravimetry alone, would be indistinguishable from the unmodified gum.

RESULTS AND DISCUSSION

After each guar gum sample had been run, the data collected was recalled from the TAGA disk storage. There are three major ways of displaying the stored mass spectral data on the TAGA system. The first way is a plot and tabulation of each scan with or without background subtraction. This method provides the temperature mass spectral correlation. The second

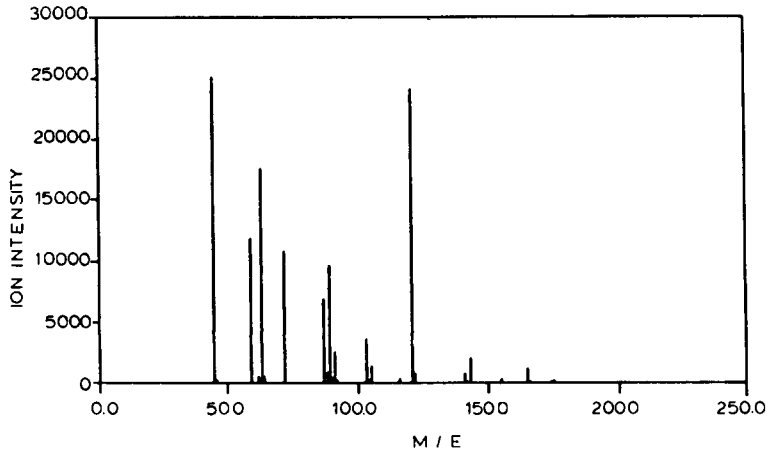

Fig. 12. Averaged mass spectrum. Glyoxal guar.

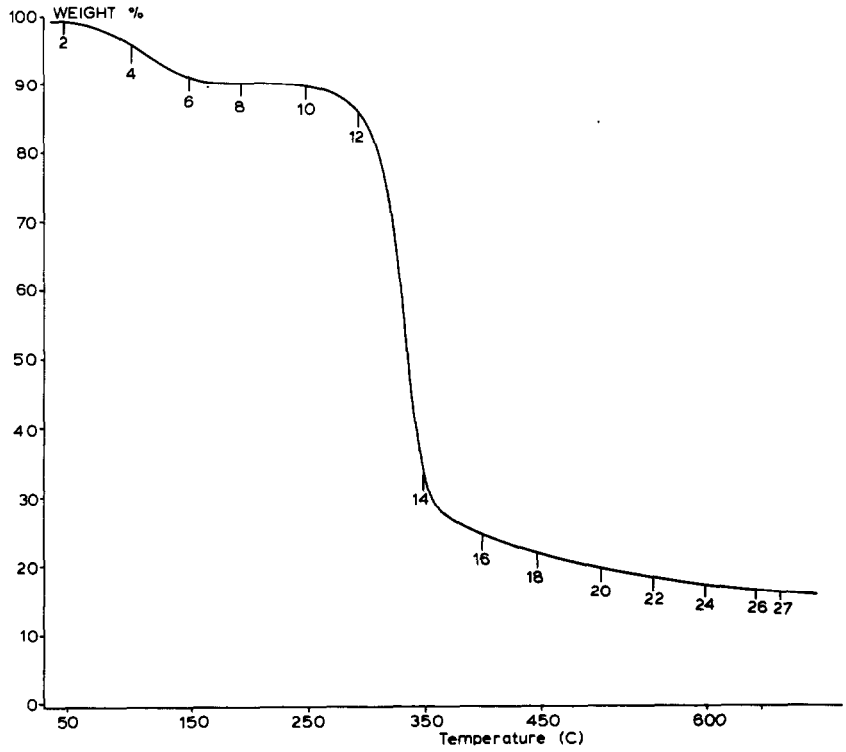

Fig. 13. Mass spectra–mass loss curve correlation for food grade guar gum.

method plots four selected ions at a time over the sequence of scans specified. The third method takes a numerical average of the specified sequences and gives an "average" spectrum with or without background correction.

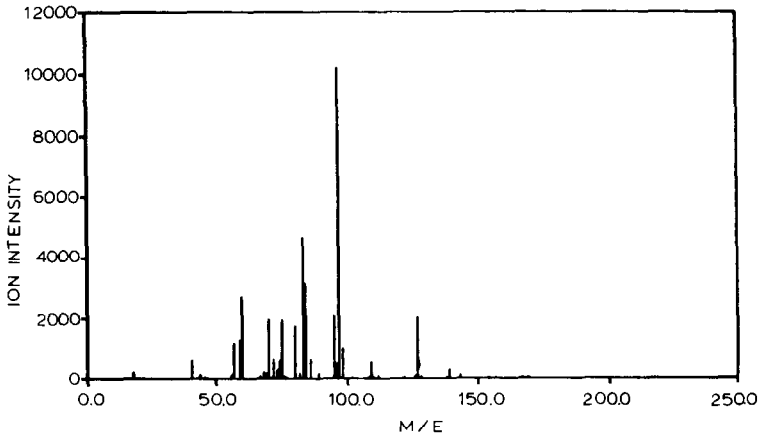

Fig. 14. Mass spectrum produced at 325°C. Background subtraction of spectrum at 50°C for food grade guar gum.

TABLE 3

Most intense ions produced at 325°C

Gum	*m/e*				
FG	97	83	84	60	95
G	60	127	80	86	72
HE	121	80	59	89	86
HP	97	111	80	83	86
SCE	111	97	125	80	83
SCM	111	97	83	80	125
TMHP	60	80	94	74	88

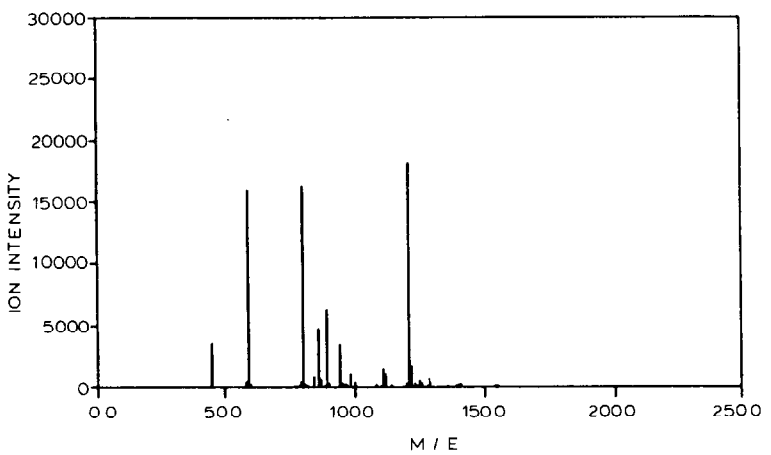

Fig. 15. Mass spectrum produced at 325°C. Background subtraction of spectrum at 50°C for hydroxyethyl guar.

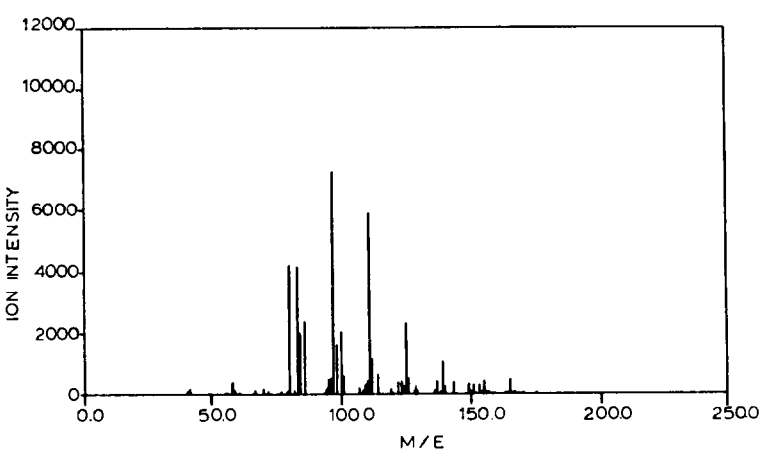

Fig. 16. Mass spectrum produced at 325°C. Background subtraction of spectrum at 50°C for hydroxypropyl guar.

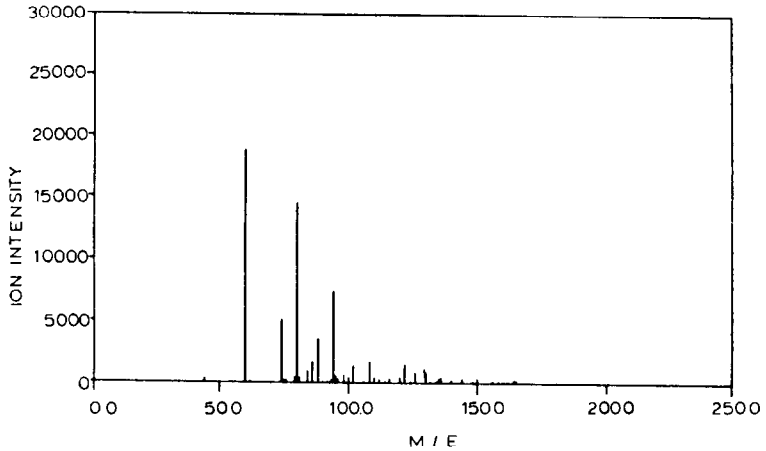

Fig. 17. Mass spectrum produced at 325°C. Background subtraction of spectrum at 50°C for 3-trimethylamino-2-hydroxypropyl guar chloride.

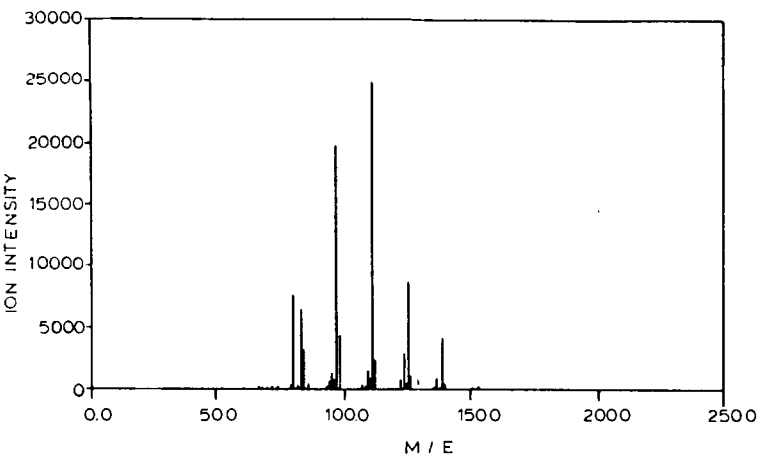

Fig. 18. Mass spectrum produced at 325°C. Background subtraction of spectrum at 50°C for sodium carboxyethyl guar.

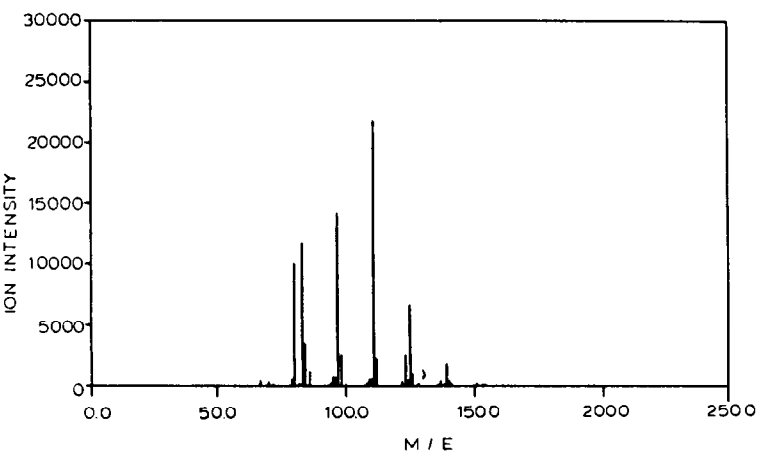

Fig. 19. Mass spectrum produced at 325°C. Background subtraction of spectrum at 50°C for sodium carboxyethyl guar.

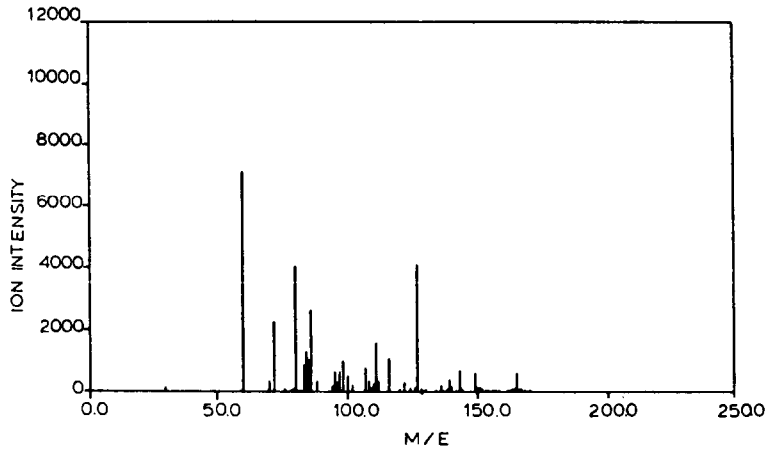

Fig. 20. Mass spectrum produced at 325°C. Background subtraction of spectrum at 50°C for glyoxal guar.

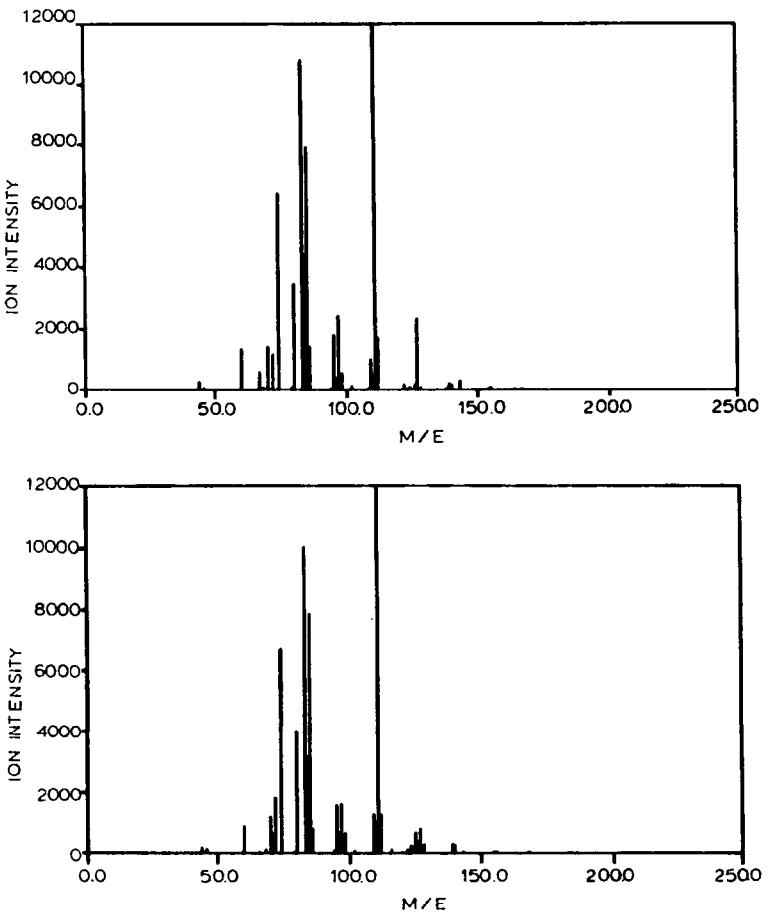

Fig. 21. Reproducibility of ion fragmentation and collection for two food grade guar gum samples.

The averaged mass scans were used to demonstrate differences between the modified guar and the unmodified food grade guar. The averaged mass spectra of the food grade guar was subtracted from that of each of the modified guars. The mass spectral differences attributed to the chemical modification are shown in Figs. 7–12.

While these differences are sufficient for a screening process, the power of the combined TG–TAGA system is better demonstrated using the single spectrum plot which is time and temperature specific. Figure 13 displays a typical guar gum TG curve and the time–temperature location of selected mass scans. Figures 14–20 compare the mass spectrum for the pyrolysis products at 12 min into the run for each of the guar gums. In this case, the background correction was made by subtracting the second scan in the run (at 50°) from the scan at 325°C. Each of the gums produced a different mass spectrum at this temperature.

Table 3 tabulates the five most abundant ions from the 12th scan for each of the gums. Figure 21 compares two mass scans from replicate runs of food grade guar gums, which illustrate the reproducibility of ion fragment production and collection.

CONCLUSIONS

We have developed a new combined thermogravimetric–atmospheric pressure ionzation mass spectrometry technique which is useful for comparing complex sample matrices where thermogravimetric data is insufficient. The simplicity of interface fabrication for this system of the PE TGS-2 and the Sciex TAGA 3000 has been demonstrated. Through the use of this combined technique, further understanding into the processes of thermal pyrolysis and degradation are possible through the mass spectral analysis of the effluent.

NOTE

Mention of a specific brand name does not consititute a recommendation by the U.S. Customs Service.

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