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Manipulation of ion trap parameters to maximize compound-specific information in gas chromatographic–mass spectrometric analyses

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ABSTRACT

The most effective way to conduct trace analyses of complex samples is to couple a high-resolution separation method to a sensitive, information-rich detector. The latest generation quadrupole ion trap uses an automatic gain control (AGC) scan function and an axial modulation voltage to achieve maximum sensitivity. With these capabilities, an ion trap gas chromatography–mass spectrometry system can separate, quantitate, and identify low picogram quantities of trace analytes present in a complex sample.

The AGC scan function uses a target value (AGC-TV) during analysis to maximize signal intensity by varying ionization time. Filament emission current (FEC) is also a major affector of ion trap signal intensity when electron ionization (EI) is used. Maximum sensitivity was achieved when AGC-TV and FEC were optimized. Additionally, useful information about selected types of compounds were also obtained from analyses conducted with non-optimum AGC-TV and FEC settings. In these specific cases, the effects seen when non-optimal AGC-TV or FEC settings were used could be explained in terms of the inherent ion chemistries of the compounds.

INTRODUCTION

The power of mass spectrometry (MS) as a detection method lies in the enormous amount of useful information it provides [1]. In routine use, searching a library of "known" spectra allows for rapid identification of unknowns in a capillary gas chromatogram. For trace analysis, this technique is limited only by the ability of the instrument to obtain a characteristic spectrum from a small amount of sample. This ability is affected primarily by instrument design limitations and by variations in ion chemistry.

The ion trap mass spectrometer has rapidly developed into an extremely valuable analytical tool [2,3] and the earliest versions of commercial ion traps were valued for their sensitivity. However, they exhibited certain instrumental design limitations that were often incorrectly attributed to ion chemistry [4]. Continued development of the ion trap corrected these early design limitations [5] and its latest generation (Saturn) provides maximum sensitivity. The remaining affector of spectral characteristics, thus, is inherent ion chemistry. Specific compounds naturally undergo ion-neutral reactions under electron ionization (EI) conditions which are independent of instrument type [6]. This behavior can provide useful information [7] as long as the spectra are consistent enough for library searching. For example, significant M + 1 formation in the spectra of fatty acid methyl esters (FAMEs) allowed identification of the molecular ion in addition to library confirmation [8].

In addition to sample concentration, major variables of ion trap EI-MS are automatic gain control-target value (AGC-TV) and filament emission current (FEC). These parameters were characterized in this work to optimize library identification capa-

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bilities and to allow additional information about inherent ion chemistries to be obtained.

EXPERIMENTAL

The ion trap system [Varian Saturn gas chromatography (GC)–MS System] utilized a temperature-programmable, cold on-column injector (Varian SPI) and a 25 m × 220 μm, HT5 capillary column (SGE) with a 0.25-μm film thickness to separate analytes of interest. The carrier gas velocity (helium) was approximately 30 cm/s and various column oven programs were used to achieve suitable separation of selected test samples (PolyScience). The transfer line was held at 280°C and the ion trap manifold was set at 260°C. The ion trap was first tuned using default software settings to obtain suitable mass calibrations and electron multiplier responses. FEC and AGC-TV settings were subsequently manipulated as indicated below. For all analyses, the injector used a high-performance insert and was programmed as follows: 0.1 min at 40°C, 150°C/min ramp to 280°C, hold until end of column program.

RESULTS AND DISCUSSION

Quadrupole ion traps use an AGC scan function (Fig. 1) to conduct mass analyses. Ions are trapped and subsequently ejected by ramping the radio frequency (RF) voltage applied to the ring electrode. Ions with low m/z sequentially eject before higher m/z ions as the RF voltage increases. Before a "spectrum" scan occurs, the system first uses a fixed ionization time and a rapid RF scan to get a gross measurement of the sample size [the "base" total ion current (TIC) measurement]. Using both the "base" TIC measurement and the AGC-TV, the ionization time for the mass analysis can then be adjusted by the system in real time to achieve the desired signal level. Thus, the higher the AGC-TV for a given sample size, the longer the actual ionization time. Because longer ionization times allow more ions to be produced from a given sample, increasing the AGC-TV is an effective way to increase signal intensity. FEC also affects signal intensity, but does so independent of time. A higher FEC causes more electrons to be injected into the trap during ionization, and this increases the production of sample ions (and their signal intensity). In this situation, if the AGC-TV remains unchanged, the AGC scan function will respond to the increased signal by shortening the ionization time.

In this system, changing FEC had a greater effect on signal intensity than did changing the AGC-TV (Fig. 2). The relative relationships shown for m/z 69 of DFTPP were generally found in all other analyses. Increasing AGC-TV was a practical way to in-

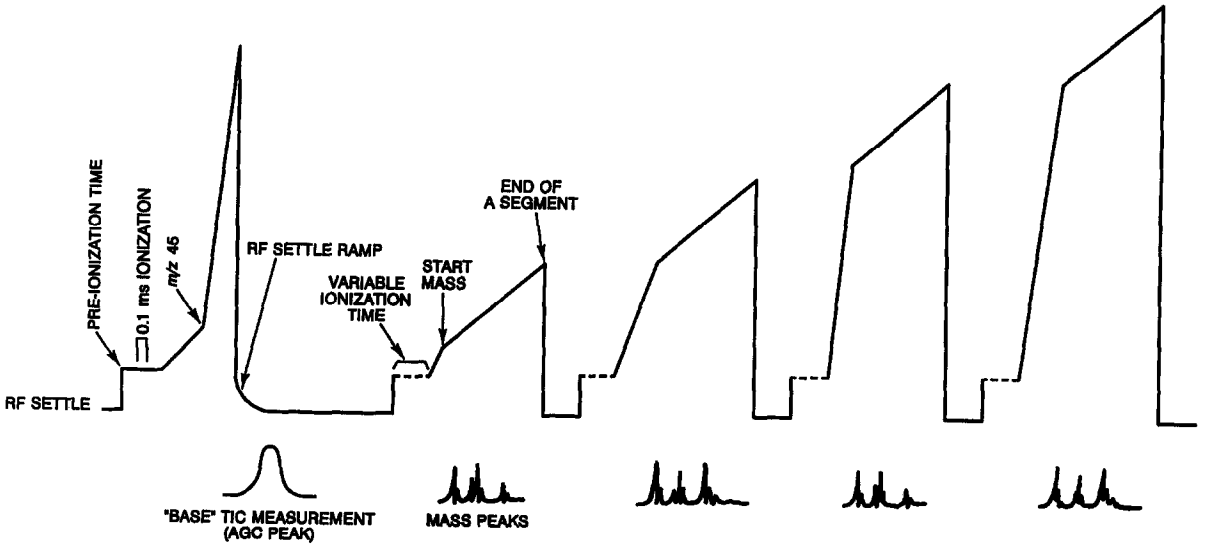

Fig. 1. The AGC scan function.

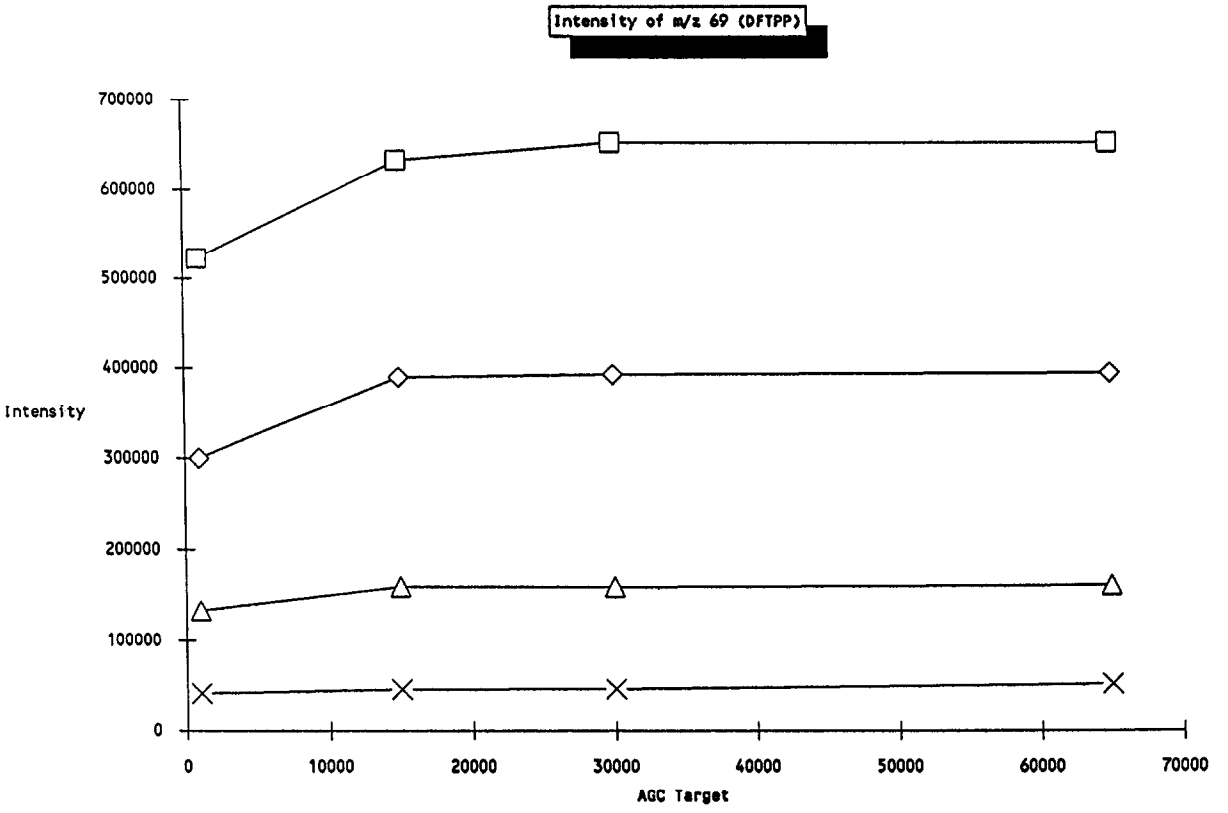

Fig. 2. Effects of AGC-TV and FEC on ion intensity. FEC: × = 10 μA; △ = 25 μA; ◇ = 50 μA; □ = 100 μA.

crease signal intensities, however, the greatest effects were seen for changes below 30 000. The major affector of signal intensity was FEC and its effects were significant throughout the instrument's operational range. In practical terms, a FEC of 50 μA and an AGC-TV of 25 000 provided excellent sensitivity without excessive loss in filament lifetime. Under these conditions, low picogram quantities of sample gave library searchable spectra (*e.g.*, with commercial EI spectral libraries).

In the spectra of certain analytes, M + 1 ions were observed which resulted from ion-neutral interactions. Compounds that were prone to M + 1 formation could be grouped into two categories based on both their spectral characteristics and their reaction to AGC-TV and FEC manipulation. "Type 1" compounds had "weak" molecular ions (*i.e.*, of low relative abundance) and included FAMEs, amphetamines, benzodiazepines, and barbiturates. The spectra of "Type 1" compounds were generally unaffected by changes in AGC-TV or FEC. "Type 2" compounds had "stronger" molecular ions (*i.e.*, of greater relative abundance) and included atrazine, ketones, imides and triazines. AGC-TV and FEC could be used to affect the relative extent of M + 1 formation for "Type 2" compounds. The inherent

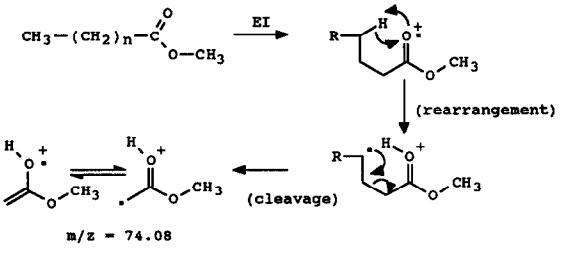

Fig. 3. Formation of the major proton-donating ion in electron ionization of fatty acid methyl esters.

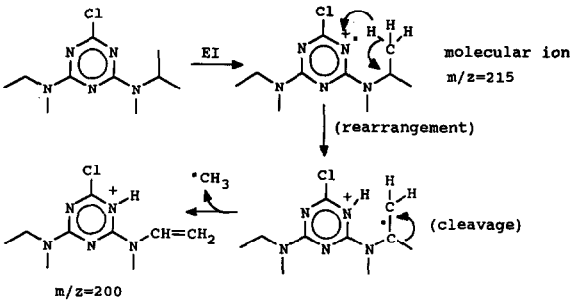

Fig. 4. Formation of the major proton-donating ion in electron ionization of atrazine (molecular mass 215).

ion chemistries of both types of compounds caused them to produce significant amounts of proton donating ion fragments under EI conditions. These fragments protonated the neutral molecules to form M + 1 ions. The general sequence could be described as follows:

$$AB \xrightarrow{(1)} AB+$$

$$AB+ \xrightarrow{(2)} AH+ \text{ and } B$$

$$AH+ \text{ and } AB \xrightarrow{(3)} ABH+ \text{ and } A$$

(1) Electron ionization of the neutral compound (AB) produced the molecular ion (AB+).

(2) Rearrangement and cleavage of the molecular ion (AB+) produced the proton donating ion (AH+).

(3) The proton donating ion (AH+) protonated a neutral sample molecule (AB) which became the M + 1 ion (ABH+).

For example, the base peak (most abundant ion) for many FAMEs ("Type 1") is an ion with *m/z* 74. This ion is a strong proton donor which is formed as shown in Fig. 3. The base peak (*m/z* 200) for atrazine ("Type 2") is also a strong proton donor (Fig. 4). The mechanisms of EI for all the ion-neutral reactive compounds were similar, and major ions (proton donators) responsible for M + 1 formation in other samples are shown in Fig. 5.

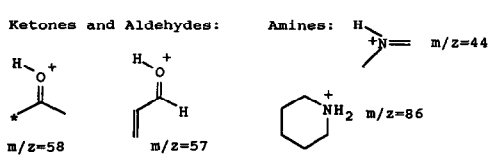

Fig. 5. Examples of proton-donating ions produced by electron ionization of ketones, aldehydes and amines.

Generally, AGC-TV and FEC had little or no effect on compounds with weak molecular ions. However, this was not considered a limitation because M + 1 was useful (in these cases) for molecular ion identification. For example, the M + 1 ion (*m/z* 187) for C-10 FAME was the only ion that significantly changed with concentration (Fig. 6). These spectra gave good library search results and demonstrated that the molecular mass for this compound was 186.

The effects of AGC-TV and FEC on compounds with stronger molecular ions was clearly seen in the spectra (Figs. 7–10) taken from 1-ng samples of atrazine (molecular mass 215). At a low FEC (10 μA), the relative abundance of the ion at *m/z* 216 (M + 1) was much lower at a low AGC-TV of 5000 (Fig. 4) than with an AGC-TV of 40 000 (Fig. 5). When a high FEC (50 μA) was used, relatively less M + 1 was formed (Figs. 9 and 10) and the effects of AGC were much less dramatic.

Differences seen in how AGC-TV and FEC affected the formation of M + 1 could be explained in terms of the relative rates of the previously described steps (1), (2), and (3). For weak molecular ion compounds (Type 1), reactions 1–3 occurred very rapidly and could be considered to be "spontaneous" relative to each other. In other words, they all rapidly approached a pseudo-equilibrium within the variable time frame of the AGC scan. The absence of a rate-limiting step for Type 1 compounds, then, is why the relative amounts of M + 1 [ABH+] was almost independent of AGC-TV (reaction time) and FEC (number of ionization electrons). These instrumental variables did affect the "amount" of total EI reactions, but not the "relative amounts" of individual products from reactions 1–3. The only way to affect the relative amount of M + 1 [ABH+] was to alter the relationships between reactions 1–3. This could be accomplished by varying the amount of sample [AB] as demonstrated in Fig. 6.

A "rate limiting step" was present for "Type 2" compounds, conversely, and their stronger molecular ion (relative to Type 1 compounds) pointed towards possible differences in how a Type 2 molecule [AB] might have reacted. Reaction 3 (protonation) was affected by reaction time (AGC-TV) and the number of ionization electrons (FEC) and, thus, was "slow" relative to the "spontaneous" reactions

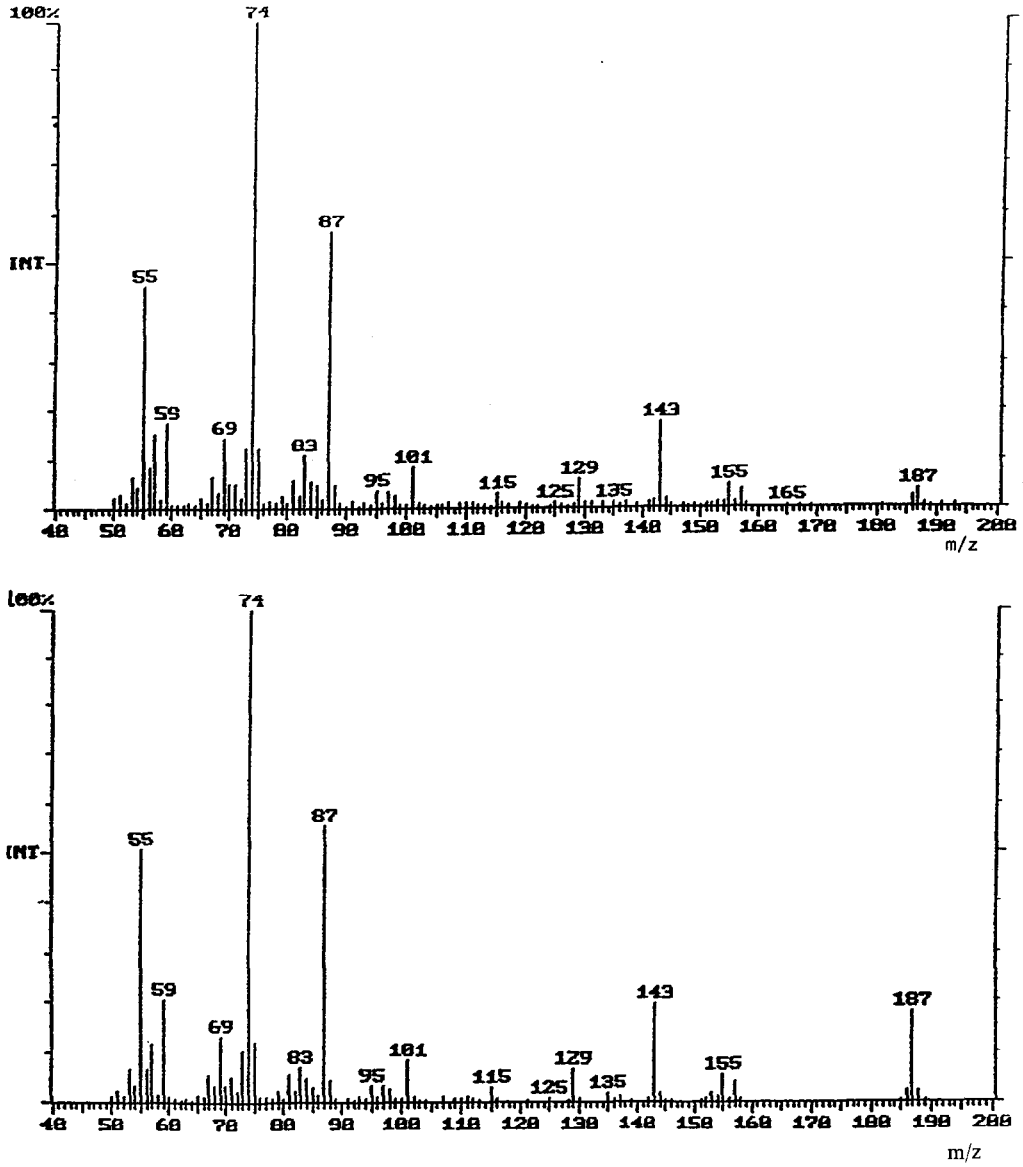

Fig. 6. Ion trap EI Spectra of C-10 FAME for 11 pg (top) and 14.4 ng (bottom) samples. Int = Intensity.

1 (EI) and 2 (rearrangement and cleavage). A change in AGC-TV affected the amount of time available for M + 1 formation. The longer reaction times at high AGC-TV created a situation similar to the Type 1 case where the three reactions were spontaneous (equilibrated) within the time frame of the AGC scan. When the rate limiting step was given more time, more of its product (M + 1) was produced relative to the other "equilibrated" products from reactions 1 and 2.

When FEC was high for Type 2 compounds, the relative amounts of M + 1 [ABH +] was lower. FEC affected reactions 1 and 2 just like it did for Type 1 compounds; it increased the total amount of their products without any relative differences. Because reaction 3 was a slower, secondary reaction, how-

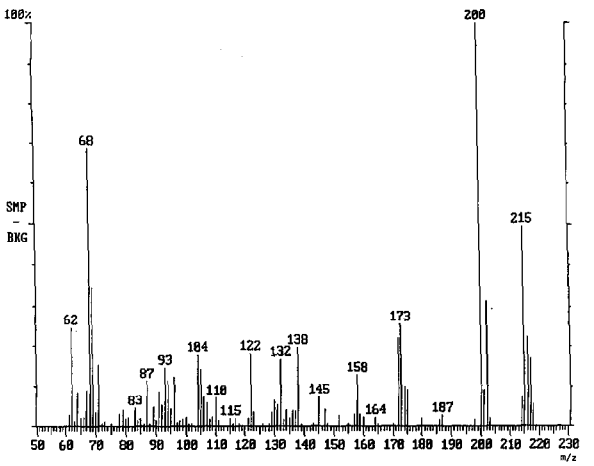

Fig. 7. Atrazine spectrum obtained using a FEC of 10 μA and an AGC-TV of 5000. (SMP-BKG means that this is a background-subtracted spectrum.)

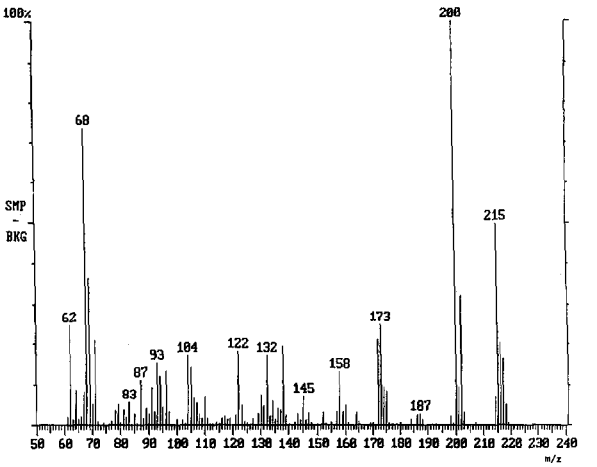

Fig. 9. Atrazine spectrum obtained using a FEC of 50 μA and an AGC-TV of 5000.

ever, FEC did not increase M + 1 formation as much as it did the formation of [AB+] and [AH+]. Although more actual M + 1 was formed at higher FEC, relative to the other EI reaction products, [ABH+] appeared to go down. Last, M + 1 formation in Type 2 compounds was also affected by sample concentration [AB] for the same reasons as previously described for Type 1 compounds.

CONCLUSIONS

For all analytes of interest, a "working optimum" of 50 μA for the FEC and 25 000 for the AGC-TV could be used. These instrumental settings gave ion signal intensities which allowed acquisition of characteristic mass scans at low sample concentrations. These same conditions were also effective for analysis of ion neutral reactive compounds because they minimized the relative abun-

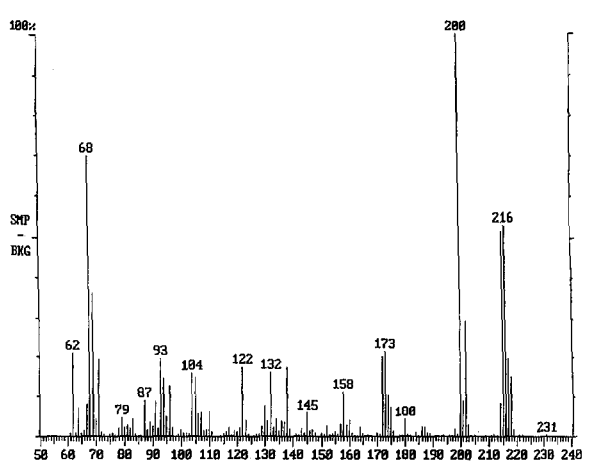

Fig. 8. Atrazine spectrum obtained using a FEC of 10 μA and an AGC-TV of 40 000.

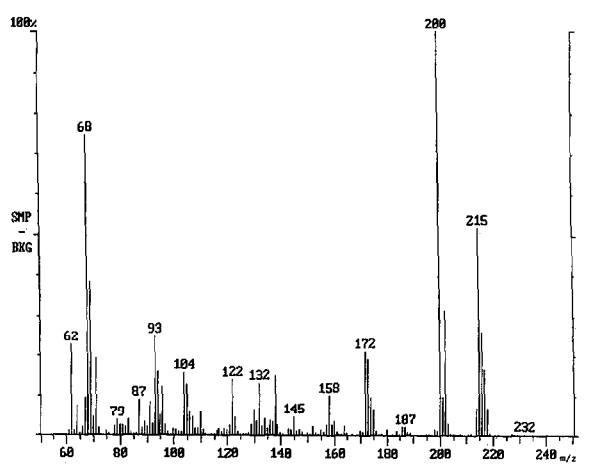

Fig. 10. Atrazine spectrum obtained using a FEC of 50 μA and an AGC-TV of 40 000.

dance of M + 1 ions in Type 2 compounds. A Type 2 unknown could be confirmed by varying either AGC-TV or FEC. Sample concentration effects were common to both Type 1 and Type 2 compounds.

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