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Thermal analysis of commercial herbicides

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Abstract

Five different plant-protecting agents (herbicides) were investigated by means of simultaneous thermal analysis/mass spectrometry.

The TA/MS experiments were carried out in air or argon atmosphere and the thermal analysis data are reported. The decomposition products released were identified by evaluation of the mass spectral data that were recorded simultaneously. The mass spectra obtained and the degradation pathways are discussed and compared with literature data.

INTRODUCTION

Large amounts of plant-protecting agents, such as herbicides, insecticides and fungicides, are used in industrial agriculture. For this reason, great quantities of these compounds are stored and transported. The physical, chemical and toxicological data (such as LD_{50} for rats and mice) for most of these substances have been determined and are reported in the literature [1-3].

In case of accidents, especially fires, it is very important to know the thermal stability of these agents and the composition of the gases released during burning processes. Therefore simultaneous thermal analysis-mass spectrometry was carried out to evaluate the thermal stability and degradation behaviour of these compounds.

EXPERIMENTAL

TA / MS equipment and measuring conditions

The simultaneous TA/MS analysis system consists of a Netzsch STA 429 thermal analyser and a Balzers QMG 511 quadrupole mass spectrometer. Two specially arranged ceramic tubes were used to achieve the pressure drop from ambient pressure to high vacuum, to permit the simultaneous recording

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TABLE 1

Materials [a]

Name	Chemical specification
Atrazine	Triazine derivate
2,4 D	2,4-Dichlorophenoxyacetic acid
Dichlobenil	Chlorinated aromatic nitrile
MCPA	Monochlorophenoxyacetic acid
Metamitron	Triazin derivate
Metoxuron	Urea derivate
Metribuzin	Triazin derivate
2,4,5 T	2,4,5-Trichlorophenoxyacetic acid

[a] All products were technical grade (90–98% purity)

of the mass spectra. The pressure was adjusted to 3.8×10^{-3} Pa and was regulated by a self-developed regulating device for the complete measurement. The ionisation occurs by means of a rhenium cross-beam ion source at 70 eV and the detection was by means of a 90° off-axis SEM.

For the experiments, samples weighing between 15 and 25 mg were placed in alumina crucibles, with MgO as reference. The heating rate applied was 5 K $\min^{-1}$ from ambient temperature to the end of the mass loss.

The MS data were processed fully by a Digital Equipment PDP 11/23 + microcomputer under an RT 11 operating system. The software package was self-developed under FORTRAN IV.

Materials

We investigated eight different herbicides. Their common names and chemical classifications are listed in Table 1.

All the investigated compounds were of technical grade and are available commercially from Promochem GmbH (Wesel, Germany).

RESULTS AND DISCUSSION

Dichlobenil

Dichlorobenzonitrile is a colourless crystalline compound. The technical product, contaminated by 9–10% of dichlorobenzamide, is light yellow. The melting point is given as 145–146 °C (418–419 K) [1].

The initial temperature (T_i) for the beginning of the weight loss at 377 K is just below the melting point of the compound. The weight loss is a one-step process to 100% with a maximum at 496 K and is related to a weak endothermic process. Table 2 lists the TA data taken in air atmosphere.

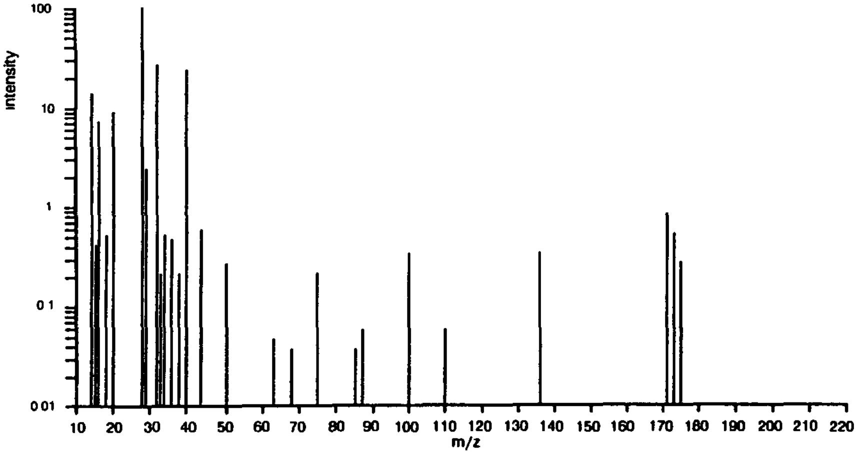


Fig 1. Mass spectrum of Dichlobenil (air atmosphere).

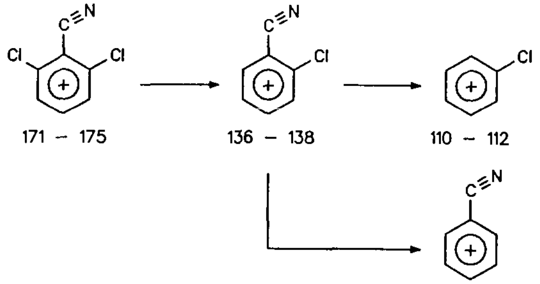


Fig. 2 Fragmentation of Dichlobenil.

These results show that the dichlobenil is evaporated without decomposition. The simultaneously recorded mass spectral data support this result. The mass spectrum, taken at the DTG maximum, is similar to that reported in the literature [4]. The molecular peaks (*m/z* 171, 173 and 175) are in accordance with the isotopic pattern of their natural abundance. Further fragments are a result of the normal fragmentation pattern (see Figs. 1 and 2).

TABLE 2

TA data of Dichlobenil

Atmosphere	T_i (K)	$\mathrm{DTG}_{\mathrm{max}}$ (K) [a]	$\mathrm{DTA}_{\mathrm{max}}$ (K)
Air	337	496	419, 496

[a] All DTA maxima are endothermic.

TABLE 3

TA data of Metoxuron

Atmosphere	T_i (K)	$\mathrm{DTG_{max}}$ (K)	$\mathrm{DTA_{max}}$ (K) [a]
Air	445	560	400, 560
Argon	449	570	396, 570

[a] All DTA maxima are endothermic.

Metoxuron

Metoxuron is a light brown powder, melting at 126–127 °C (402–403 K) [1]. The weight loss starts clearly after the melting of the substance. The process begins at 445 K with a maximum at 560 K leading to a final weight loss of 100% in one step. The DTA curve has two endothermic maxima. The first at 403 K represents the melting and the second, corresponding with the DTG maximum, the evaporation of the sample. Additional investigations in argon atmosphere gave the same results. This can be taken to indicate evaporation of the sample without any decomposition or oxidation. The results are listed in Table 3.

The reconstructed total ion current of the overall mass spectra taken (see Fig. 3) shows, in accordance with the DTG curve, one maximum at the same temperature.

The mass spectrum taken at the maximum of the total ion current (Fig. 4) shows that there is no molecular ion peak. The highest fragment that could be detected is *m/z* 183. This is Metoxuron without dimethylamine. The cleavage of dimethylamine by thermal stress is not accompanied by an oxidation of the products, as can be seen in the mass spectrum taken from the investigations in argon atmosphere (see Fig. 5). Allowing for the different evaluation and acquisition techniques, the two spectra are identical.

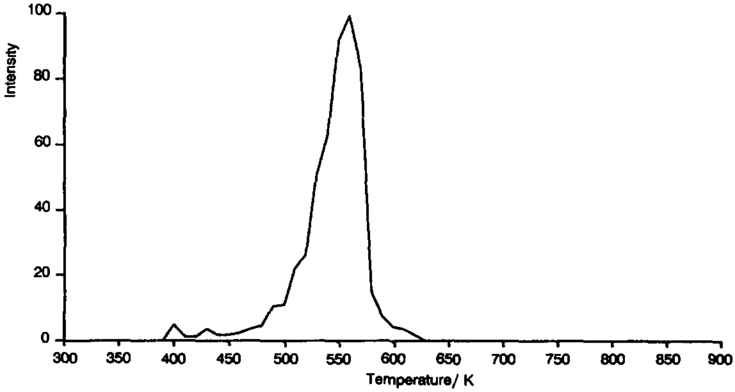


Fig. 3. Total ion current intensity of Metoxuron

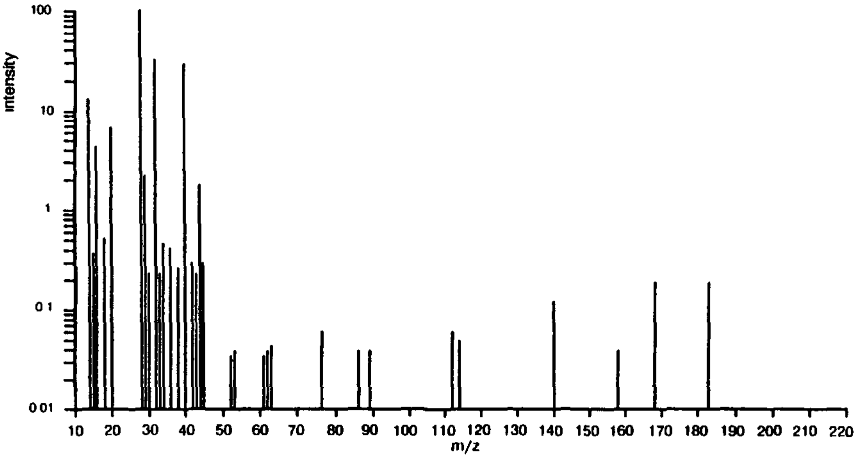


Fig 4 Mass spectrum of Metoxuron (air atmosphere)

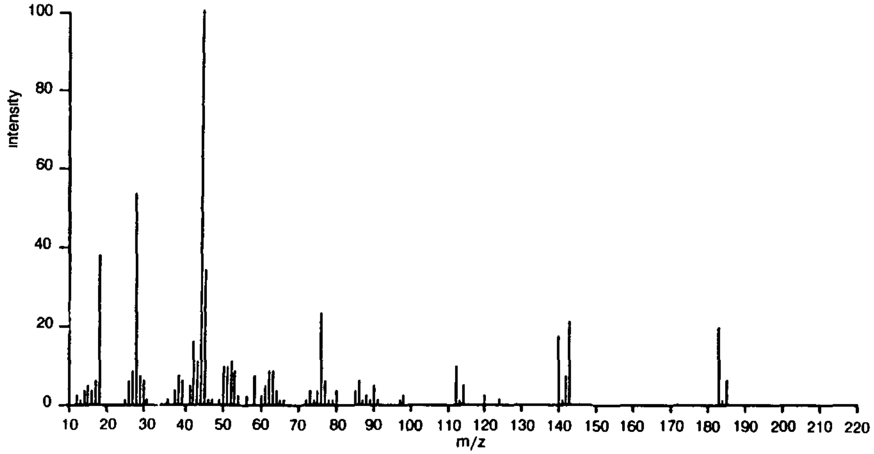


Fig. 5 Mass spectrum of Metoxuron (argon atmosphere).

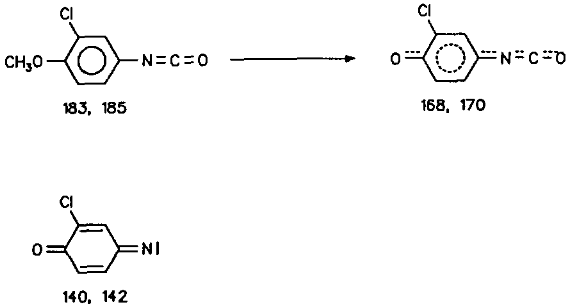
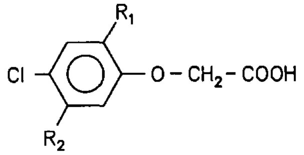


Fig 6. Fragmentation of Metoxuron



2,4 - D . R_1 = Cl, R_2 = H
MCPA R_1 = CH_3, R_2 = H
2,4,5 - T · R_1 = Cl, R_2 = Cl

Fig. 7 Structures of phenoxyacetic acid derivatives.

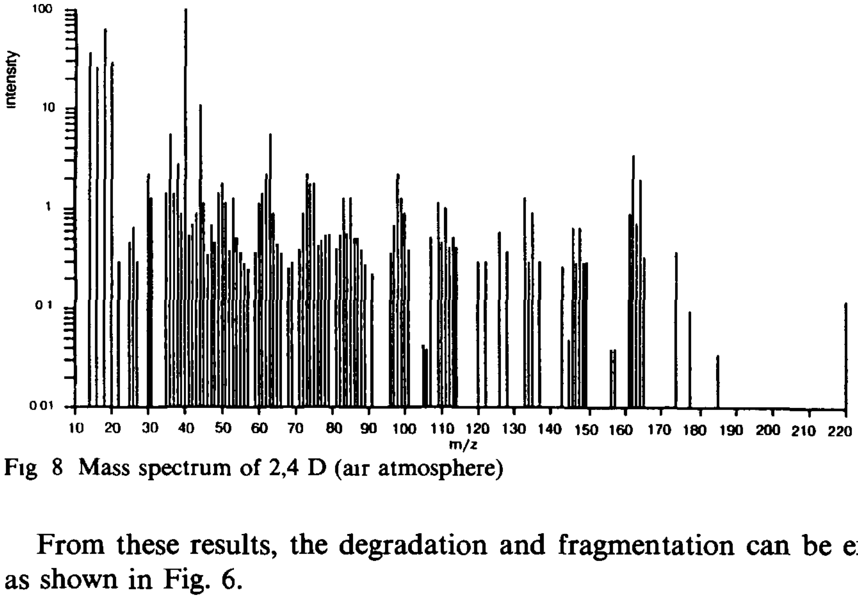


Fig 8 Mass spectrum of 2,4 D (air atmosphere)

From these results, the degradation and fragmentation can be explained as shown in Fig. 6.

Chlorinated phenoxyacetic acids (2,4 D, MCPA and 2,4,5 T)

These three substances are different derivatives of phenoxyacetic acid. The general structure of these pesticides is given in Fig. 7.

TABLE 4

TA data for 2,4 D, MCPA and 2,4,5 T in air and argon

	T_i (K)	DTG$_{max}$ (K)	DTA$_{max}$ (K)
2,4 D			
Air	389	562	411, 561
MCPA			
Air	425	549	390, 547
Argon	425	497	390, 547
2,4,5 T			
Air	442	569	424, 558

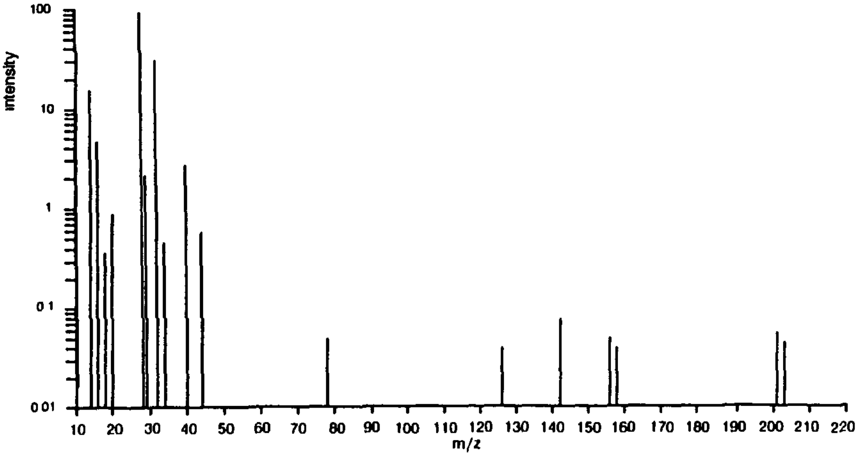


Fig 9. Mass spectrum of MCPA (air atmosphere)

The melting points given in the literature are 140.5, 118–119 and 154–155 °C (413.5, 391–392, 427–428 K), for 2,4 D, MCPA and 2,4,5 T, respectively [5].

For all the samples, the weight loss occurs in one step to nearly 100%; for 2,4 D, the process starts before the melting.

The DTA curves of all three substances have two endothermic maxima. The first is due to the melting of the substance and the second is related to the evaporation. Due to the very low intensity of the second peak, it might overlap with an exothermic oxidation of the sample. For this reason, we also investigated MCPA in argon atmosphere. These results (see Table 4) and the simultaneous mass spectrometric investigations indicate that there is no oxidation of the sample.

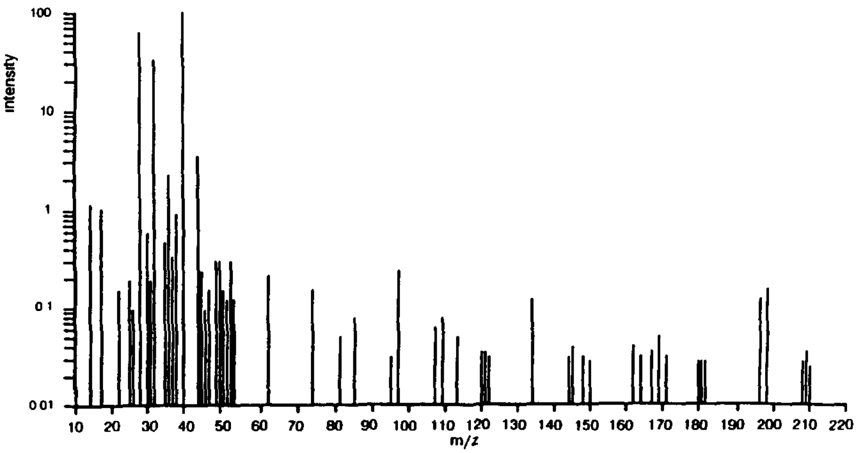


Fig. 10 Mass spectrum of 2,4,5 T (air atmosphere).

The mass spectrometric investigations of the degradation of the three substances did not show any decomposition for 2,4 D and MCPA. The mass spectra (see Figs. 8 and 9), taken from the maximum of the reconstructed total ion current, represent the molecular ion peak and are fairly similar to those in the literature [4].

The mass spectrum of 2,4,5 T (Fig. 10) does not show any molecular ion peak, in contrast to the literature report [4]. The highest fragment that could be detected is *m/z* 209, after cleaving of the carboxyl group. Further fragmentation is identical to that reported in the literature. Due to the intensity of the prominent molecular ions (*m/z* 254 and 256) it can be concluded that 2,4,5 T will decarboxylise by thermal stress.

Atrazin, Metamitron and Metribuzin

These three herbicides are triazines. Their melting points are 176, 166.6 and 125.5–126.5 °C (449, 439.6 and 398.5–399.5 K) for Atrazin, Metamitron and Metribuzin, respectively [5].

The thermal investigations of the raw materials gave unreproducible results. After grinding to a particle size of 0.05 mm diameter, the TA curves could be evaluated.

The degradation of Atrazin in air atmosphere starts before the melting of the compound and occurs in four steps to about 73%. All DTG maxima are accompanied by exothermal effects that are mostly very weak. Additional investigations in argon atmosphere have shown that a thermal, oxidative degradation takes place.

The degradation of Metamitron and Metribuzin starts after the melting of the substance and leads in one (Metamitron) and two (Metribuzin) steps to 80% and 100%. Each DTA curve shows two exothermal effects during the weight loss of the samples. Also, additional investigations in argon atmosphere have shown that there is an oxidative and thermal decomposition. The TA data are listed in Table 5.

TABLE 5

TA data for Atrazin, Metamitron and Metribuzin in air and argon

	T_i (K)	DTG_{max} (K)	DTA_{max} (K)
Atrazin			
Air	435	513, 524, 631 667	451 [a], 507, 533 621, 658
Argon	438	513, 528, 647	446 [a]
Metamitron			
Air	478	593	436 [a], 570, 598
Argon	490	588	435 [a], 579
Metribuzin			
Air	455	542, 594	400 [a], 548, 598
Argon	448	536, 593	395 [a], 540

[a] Endothermic

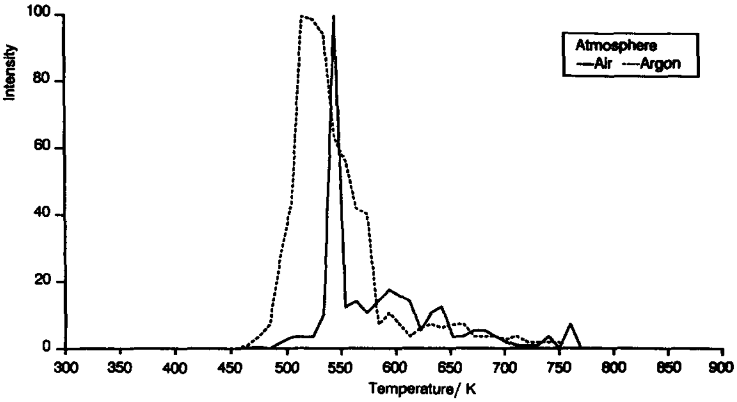


Fig. 11 Total ion current intensity of Atrazin

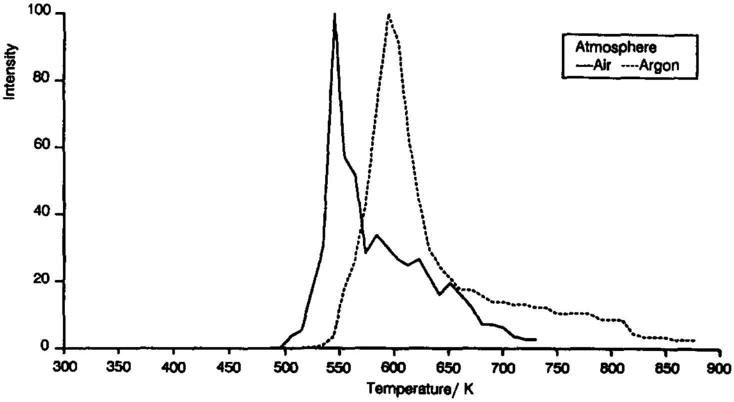


Fig 12. Total ion current intensity of Metamitron.

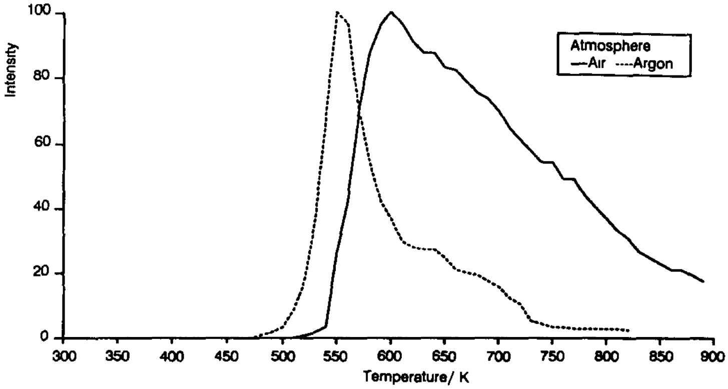


Fig. 13. Total ion current intensity of Metribuzin

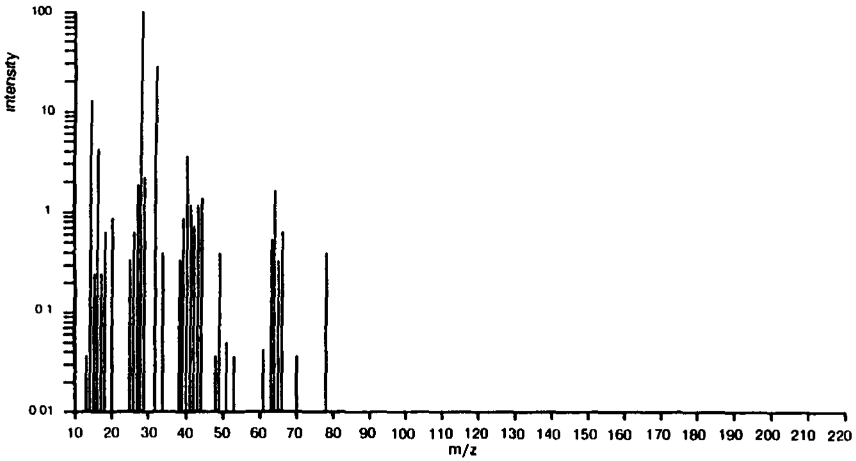


Fig. 14 Mass spectrum of Atrazin (air atmosphere)

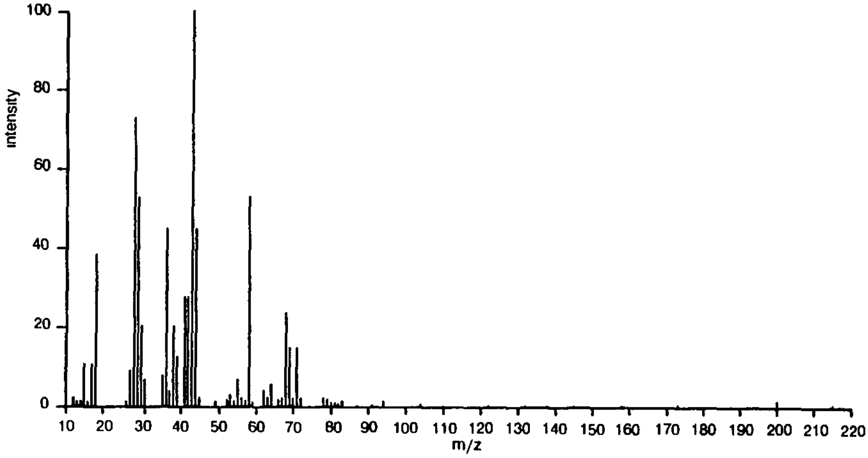


Fig 15 Mass spectrum of Atrazin (argon atmosphere).

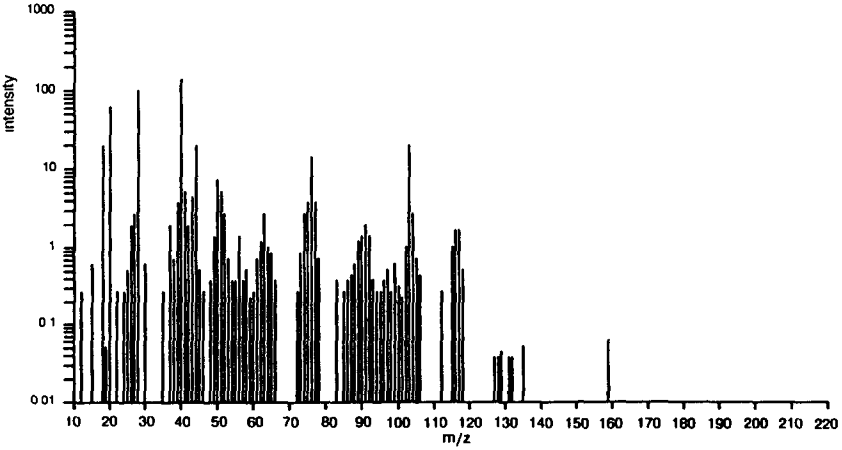


Fig. 16. Mass spectrum of Metamitron (air atmosphere).

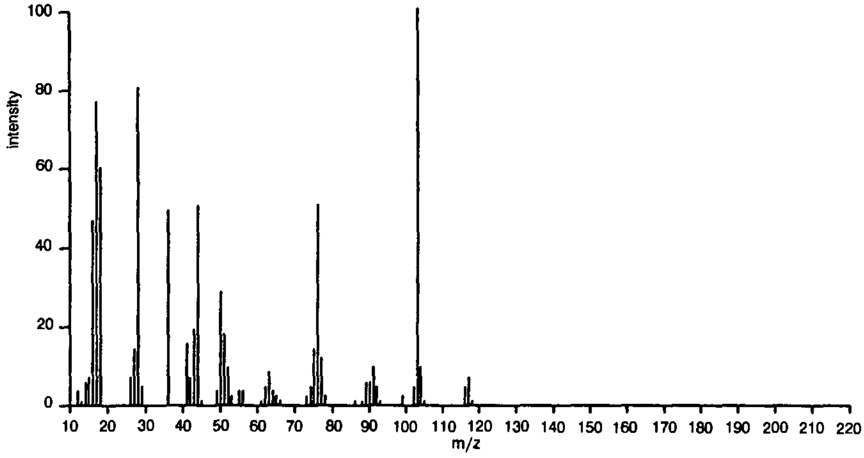


Fig 17 Mass spectrum of Metamitron (argon atmosphere).

The simultaneous mass spectrometric investigations in air and argon atmospheres also gave this result. The reconstructed total ion currents are different for air and argon atmosphere (see Figs. 11–13) and the mass spectra taken at the maxima of the curves also vary with atmosphere and are different to those described in the literature [4] (see Figs. 14–19).

From these results, the degradation of Atrazin in air atmosphere can be seen as a polycondensation of the substance by cleavage of the R–Cl bond (see Fig. 20), with $R = C_2H_5$ (m/z 64.66) or $R = C_3H_7$ (m/z 78.80) (see Fig. 14), followed by oxidation and coking of the polymer.

The degradation of Metamitron is different; an intramolecular rearrangement and decomposition occurs. (see Fig. 21).

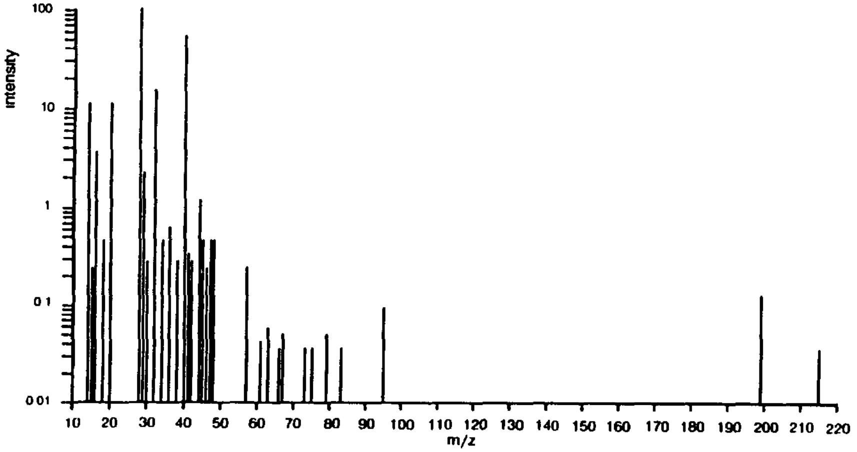


Fig. 18. Mass spectrum of Metribuzin (air atmosphere).

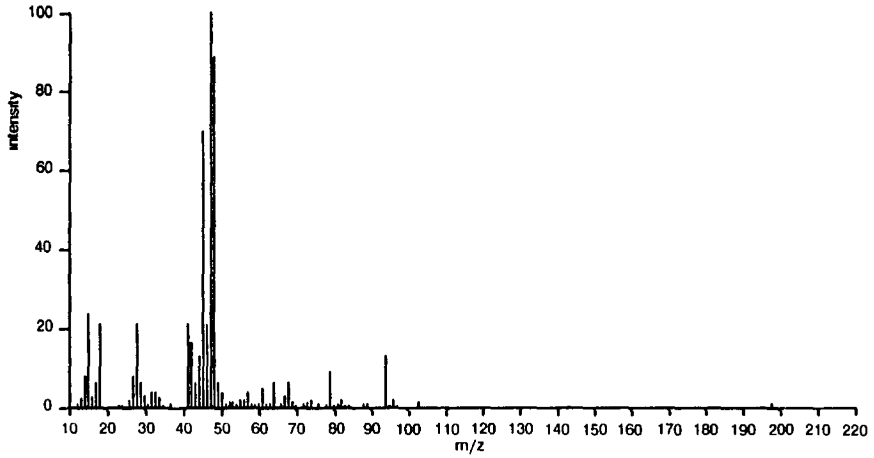


Fig. 19. Mass spectrum of Metribuzin (argon atmosphere)

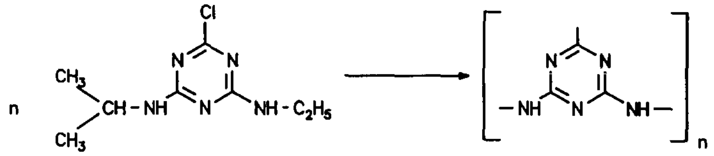


Fig. 20. Degradation of Atrazin.

Metribuzin is more stable than the other compounds: the molecular ion (m/z 214) is detected. The first fragment in the mass spectrometer is M-15 (m/z 199). Due to the absence of m/z 12 and 13 and the intensity of m/z 14 (residual gas subtracted), it can be concluded that Metamitron will loose an NH group by thermal stress. The other fragments can be explained as: m/z 94, C_3N_3O (cyclic); m/z 73, C_2H_3NS; m/z 57; C_4H_9; m/z 48, SO; and m/z 47, CH_3S.

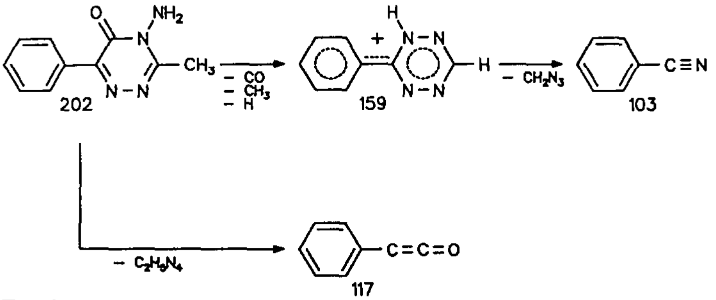


Fig. 21. Fragmentation of Metamitron.

CONCLUSION

These investigations have shown that TA/MS measurement is a helpful tool in characterising the thermal behaviour of several different plant-protecting agents. It gives information concerning the thermal stability of the herbicides and, from the simultaneous mass spectrometric investigation of the gas phase, the identification of their degradation products depending on temperature.

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