POSITIVE- AND NEGATIVE-ION MASS SPECTROMETRY OF SEVEN DINITROANILINE HERBICIDES

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原　　報

POSITIVE- AND NEGATIVE-ION MASS SPECTROMETRY OF SEVEN DINITROANILINE HERBICIDES

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ジニトロアニリン系除草剤７種類の正イオン・負イオン質量分析

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Summary

Positive ion electron impact (PIEI), positive ion chemical ionization (PICI) and negative ion chemical ionization (NICI) mass spectra are presented for seven dinitroaniline herbicides; and each fragmentation pathway has been analyzed. In the PIEI mode, molecular ions appeared for all compounds, but they were relatively small. Base or intense cations at m/z M-29, which probably correspond to $[M\text{-}C_2H_5]^+$, appeared in five compounds; $[M - OH]^+$ peaks also observed for six compounds. In the PICI mass spectra, all compounds showed intense MH^+ quasi-molecular ions, which constituted base peaks, together with small peaks at m/z M + C_2H_5 and/or M + C_3H_5; small peaks at m/z M − 33, which probably correspond to $[MH - 2OH]^+$, were observed in six compounds. In the NICI mass spectra, M^- molecular anions appeared as base peaks in all compounds. Anions at m/z $[M - 30]^-$, which may be due to loss of NO, were also observed in common for all compounds. The highest sensitivity could be obtained in the NICI mode by total ion monitoring for all compounds. The calibration curves obtained by selected ion monitoring in the NICI mode for isopropalin, nitralin and trifluralin, showed linearity in the range of 1.56−100 pg on column, with detection limits of 2−20 pg on column.

Key words: Dinitroaniline herbicides; Benfluralin; Ethalfluralin; Isopropalin; Nitralin; Pendimethalin; Profluralin; Trifluralin; Mass spectrometry; Negative ion

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Introduction

Dinitroanilines constitute an important group of herbicides being used on a wide variety of crops for the control of annual grasses and broadleaf weeds [1]. Pollution of crops and groundwater by dinitroaniline herbicides is being recognized as one of the serious environmental problems [2]. There is also a possibility of suicidal and accidental ingestion of the herbicides.

The present paper deals with positive ion electron impact (PIEI), positive ion chemical ionization (PICI) and negative ion chemical ionization (NICI) mass spectra of seven dinitroaniline herbicides, and shows very high sensitivity of NICI mass spectrometry (MS) for these compounds.

Experimental

Materials

Benfluralin, nitralin, pendimethalin and trifluralin were obtained from GL Sciences Inc. (Tokyo); ethalfluralin, isopropalin and profluralin from Supelco, Inc. (Bellefonte, PA, USA). Other common chemicals used were of analytical grade. DB-1 fused silica capillary columns (30 m x 0.32 mm i.d., film thickness 0.25 μm) were obtained from J & W Scientific (Folsom, CA, USA).

Gas chromatography (GC)/MS conditions

Mass spectra in the PIEI, PICI and NICI modes were recorded on a JEOL JMS-AX505H mass spectrometer (Tokyo) coupled to an HP5890 gas chromatograph (Hewlett-Packard Co., Palo Alto, CA, USA) with a computer-controlled data analysis system.

The MS conditions were: electron energy 70 eV, accelerating voltage 3.0 kV, ionization current 300 μA, separator temperature 250 ℃, and ion source temperature 250 ℃; in the PIEI mode, electron energy 70 eV; in the PICI and NICI modes, electron energy 200 eV, reagent gas methane and chamber pressure 1 Torr.

The GC conditions were: column temperature 50—250 ℃ (1 min hold at 50 ℃, 10 ℃/min); injection temperature 160 ℃ and helium flow-rate 3 ml/min. The samples were injected in the splitless mode at a column temperature of 50 ℃ and the splitter was opened after 1 min. Each herbicide was dissolved in methanol, and a 1-μl aliquot of it was subjected to GC analysis.

Results

PIEI, PICI and NICI mass spectra of seven dinitroaniline herbicides, and each probable fragment mode, are shown in Figs. 1—7.

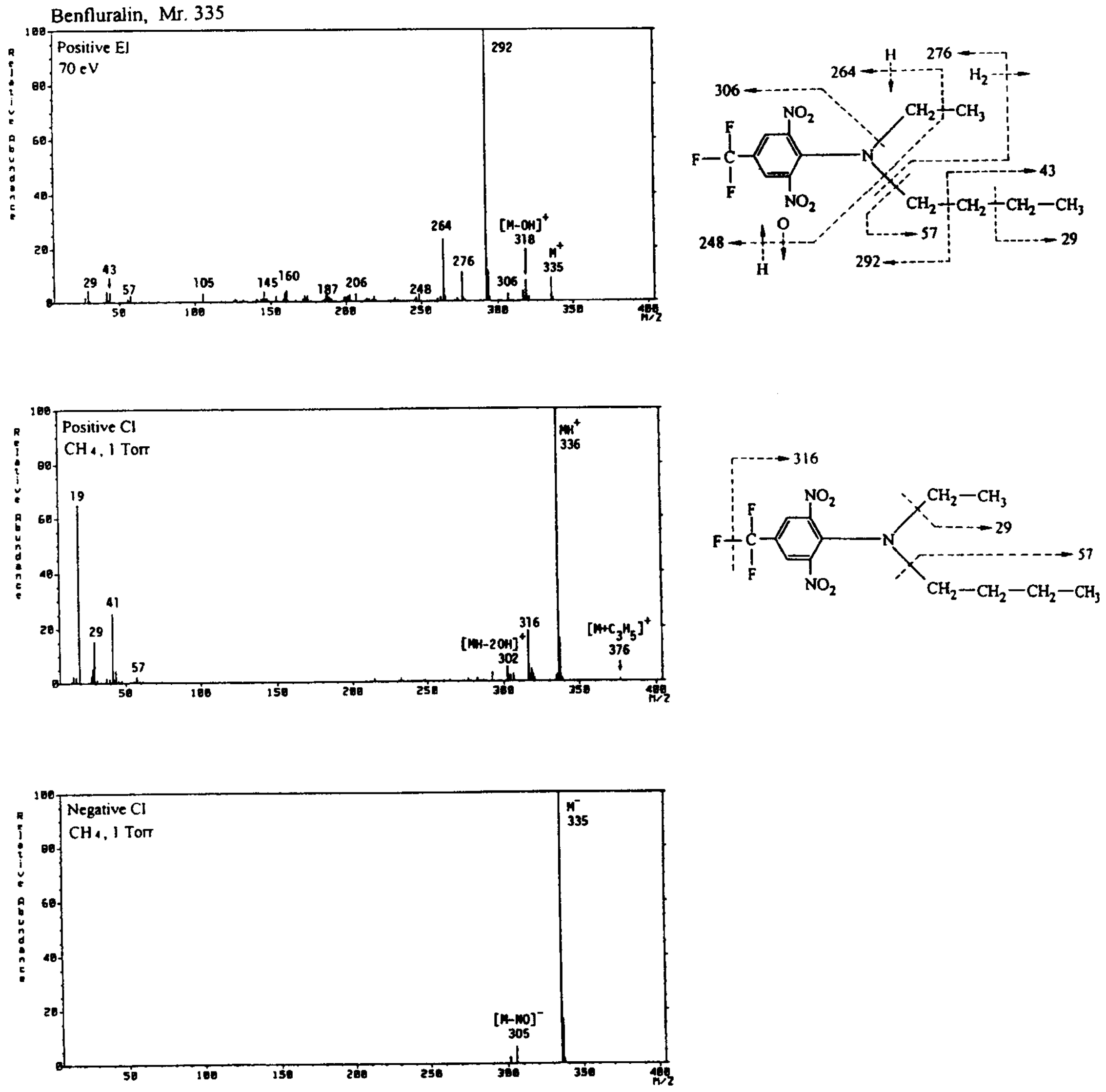

Fig. 1 . PIEI, PICI and NICI mass spectra of benfluralin and its probable fragmentation modes.

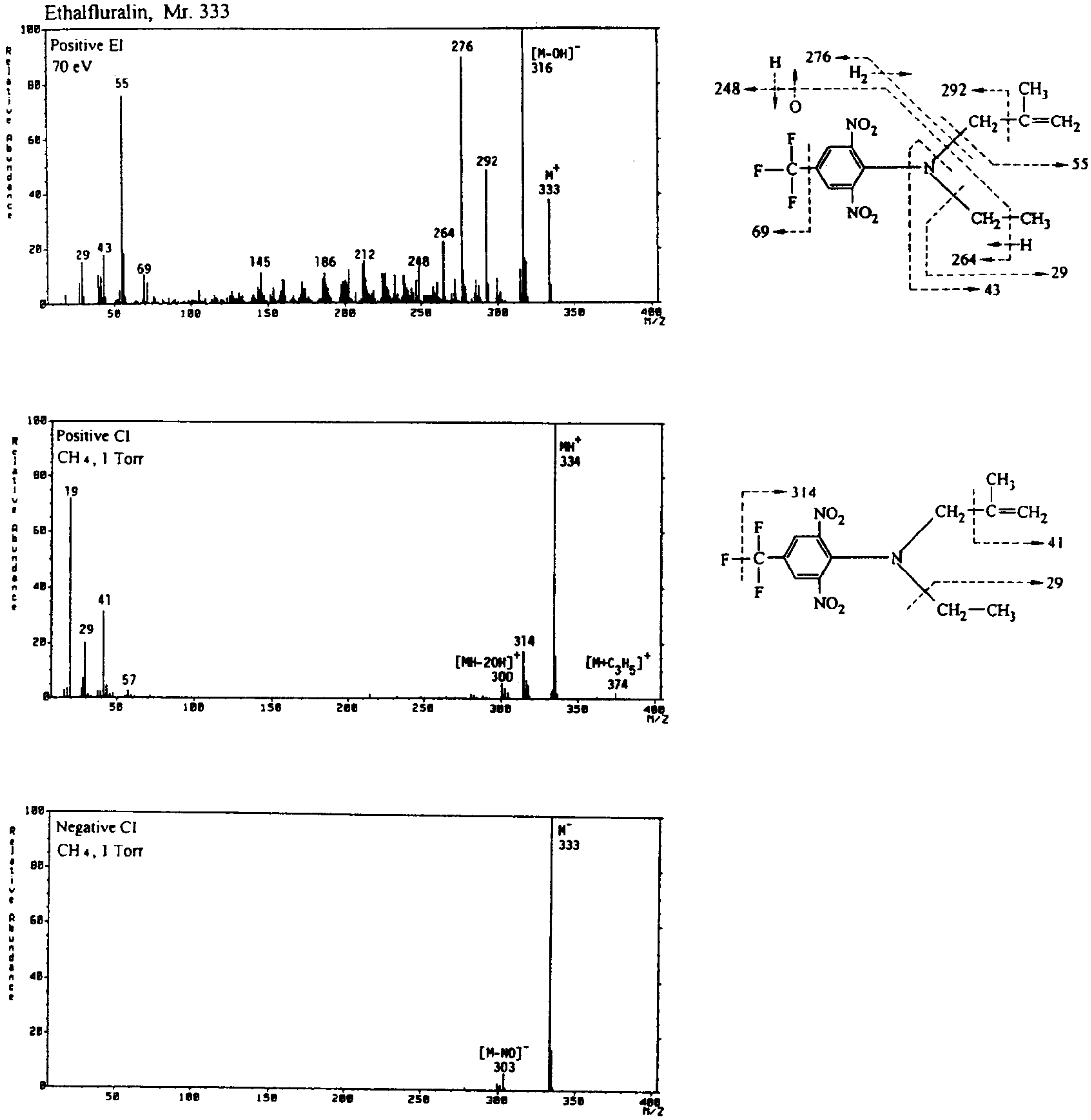

Fig. 2. PIEI, PICI and NICI mass spectra of ethalfluralin and its probable fragmentation modes.

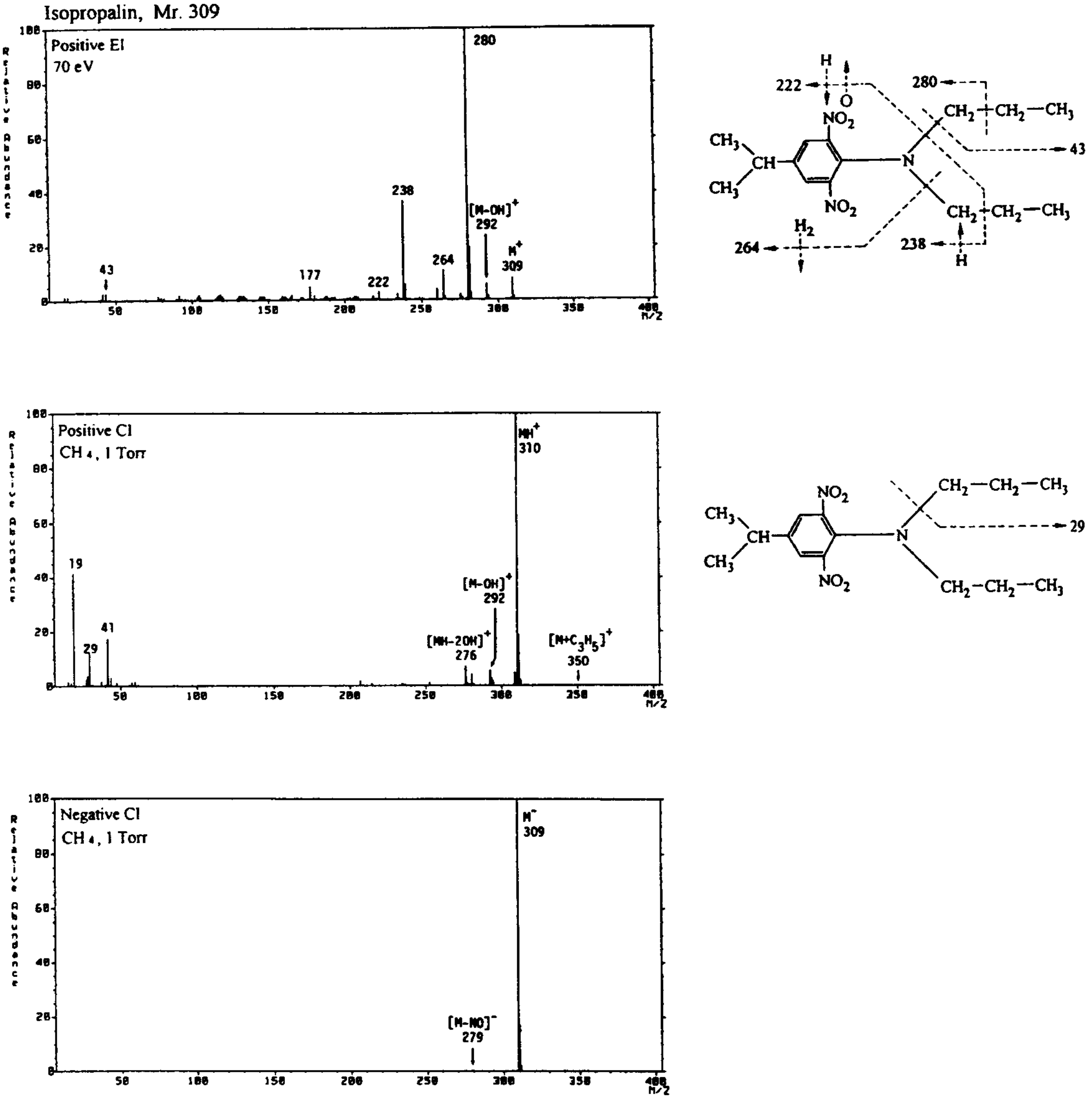

Fig. 3 . PIEI, PICI and NICI mass spectra of isopropalin and its probable fragmentation modes.

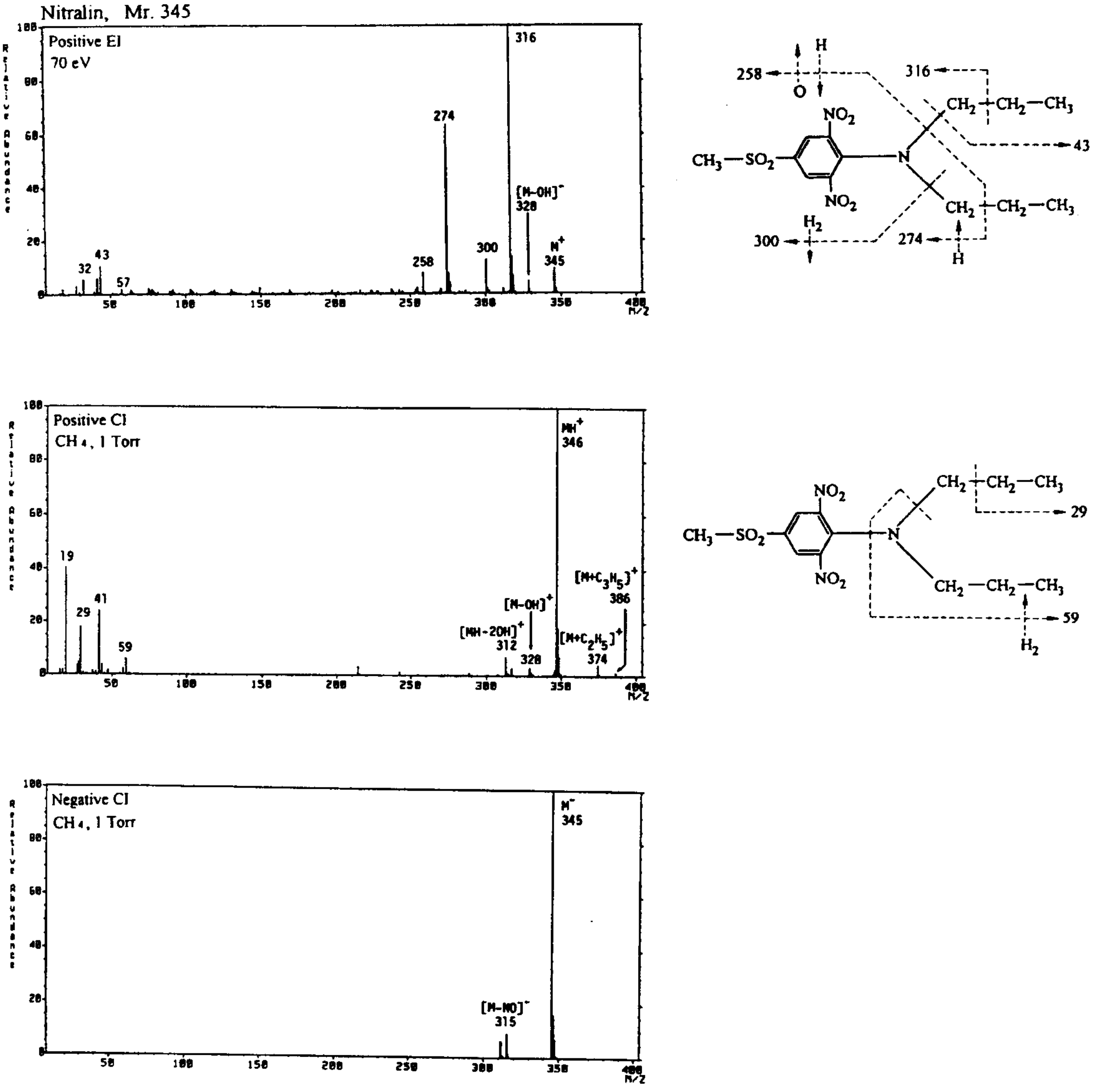

Fig. 4 . PIEI, PICI and NICI mass spectra of nitralin and its probable fragmentation modes.

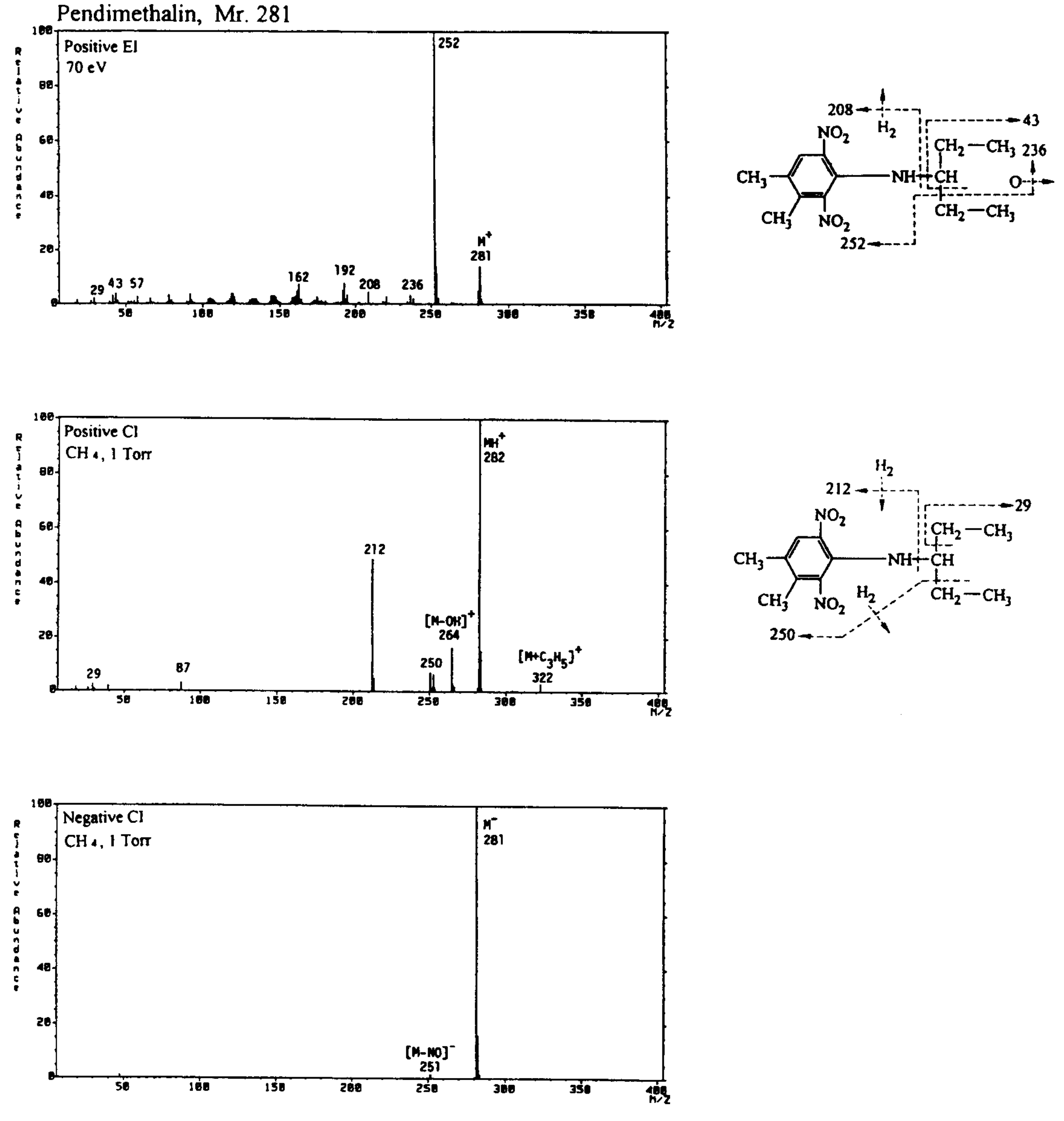

Fig. 5. PIEI, PICI and NICI mass spectra of pendimethalin and its probable fragmentation modes.

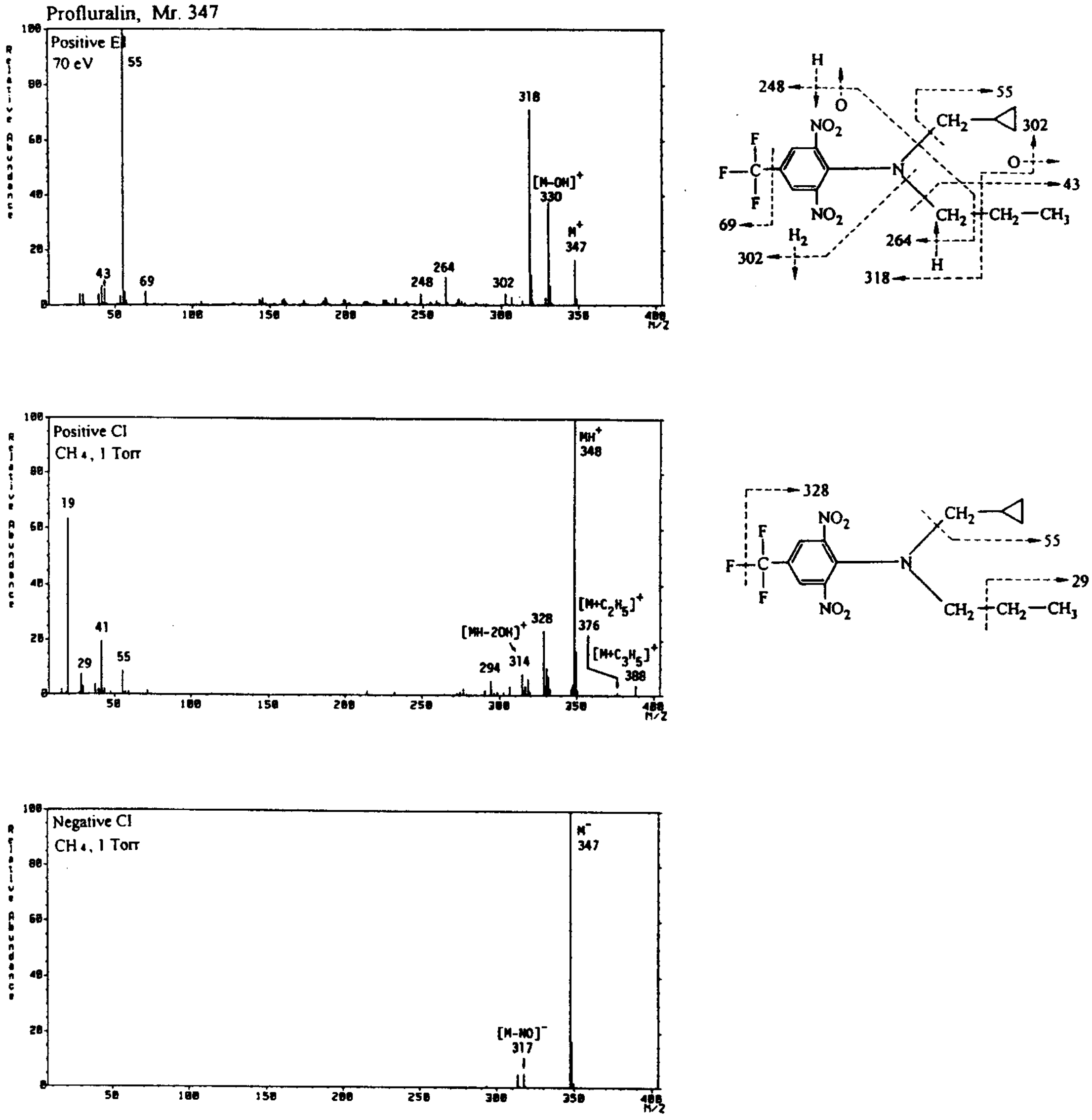

Fig. 6. PIEI, PICI and NICI mass spectra of profluralin and its probable fragmentation modes.

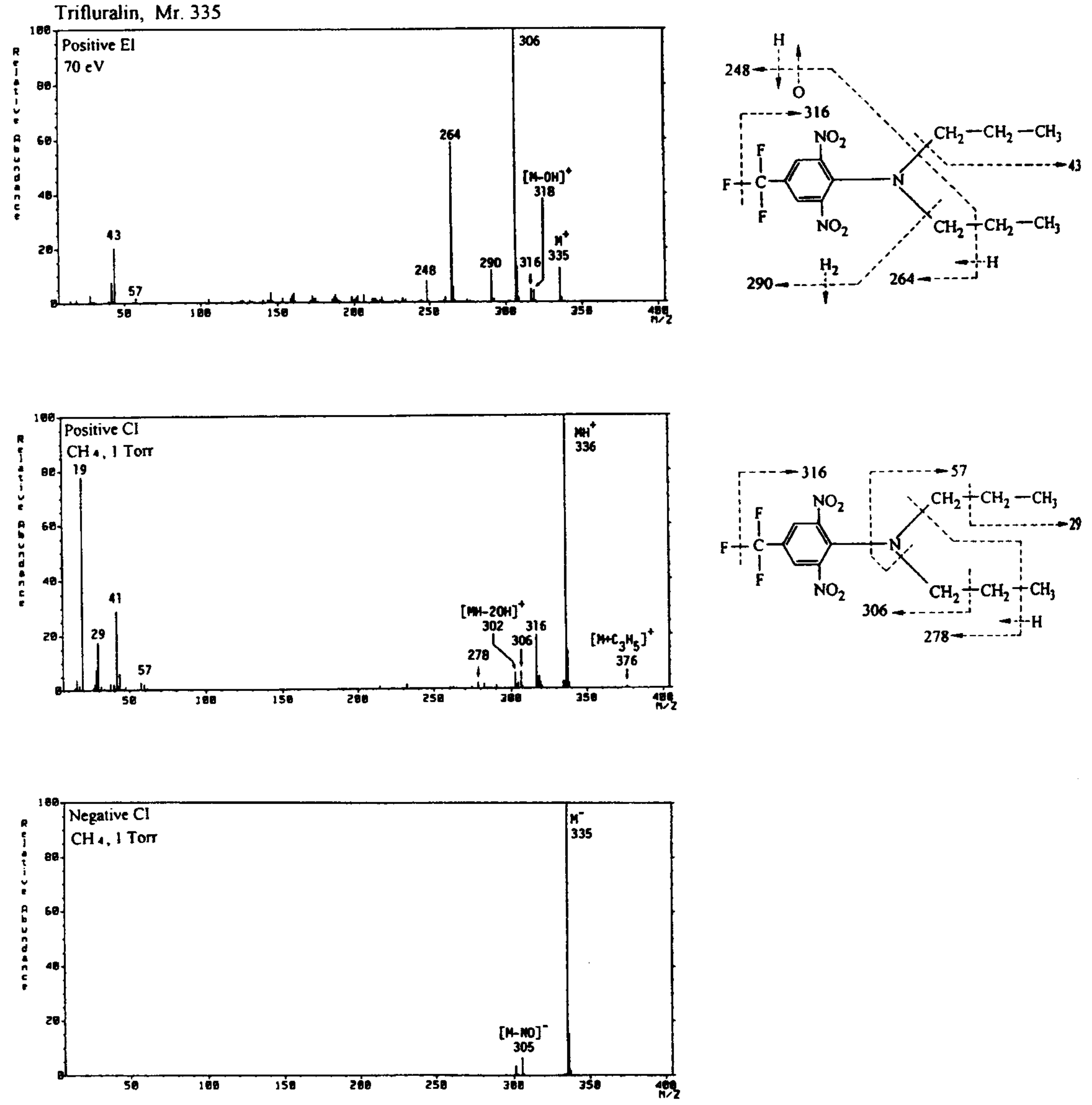

Fig. 7. PIEI, PICI and NICI mass spectra of trifluralin and its probable fragmentation modes.

PIEI mass spectra

In PIEI mass spectra, molecular ions appeared for all compounds, but they were relatively small. Cations at m/z M - 29, which probably correspond to $[M - C_2H_5]^+$, appeared for isopropalin, nitralin, pendimethalin, profluralin and trifluralin, and constituted base peaks for the compounds except for profluralin. $[M - OH]^+$ peaks also observed for six compounds. Fragment peaks at m/z 43 and 55 (or 57) were observed in common in many compounds.

PICI mass spectra

In PICI mass spectra, all compounds showed intense MH^+ quasi-molecular cations, which constituted base peaks, together with small peaks at m/z $M + C_2H_5$ and/or $M + C_3H_5$. Cations due to $[M - F]^+$ appeared for the compounds in four compounds with trifluoromethyl groups. Small peaks at m/z M - 33, which probably correspond to $[MH - 2OH]^+$, were observed in six compounds. Fragment peaks at m/z 19 (F), 29, 41 and 57 (or 55) were observed in many compounds.

NICI mass spectra

NICI mass spectra recorded for the seven herbicides were very simple; molecular anions appeared in all compounds and constituted base peaks. Anions at m/z $[M - 30]^-$, which may be due to loss of NO, was also observed in common for all compounds. No other fragment anions appeared in the chromatograms.

Sensitivity by total ion monitoring (TIM) in different modes

To check sensitivity of the present GC/MS method, the intensities of peaks obtained by TIM were compared with each other in the three modes. The detection limits for seven dinitroaniline herbicides in the PIEI, PICI and NICI modes were 1.0—4.5 ng, 5.1—20 ng and 0.05—0.3 ng on column, respectively.

Calibration curve by selected ion monitoring (SIM) in the NICI mode

Figure 8 shows calibration curves for three herbicides by SIM in the NICI mode; the molecular anions in the NICI mode at m/z 309, 345 and 335 were used for detection of isopropalin, nitralin and trifluralin, respectively. The compounds were measured against pendimethalin (m/z 281, 500 pg on column) as internal standard. They showed linearity in the range of 1.56—100 pg on column. The equation and r values for the curves were: $y=0.1097x + 0.0138$, $r=0.9992$ for isopropalin; $y=0.0196x + 0.0027$, $r=0.9999$ for nitralin; $y=0.0994x + 0.0069$, $r=0.9998$ for trifluralin. The detection limits for isopropalin, nitralin and trifluralin were 2.5—5 pg, 10—20 pg and 2—4 pg on column, respectively.

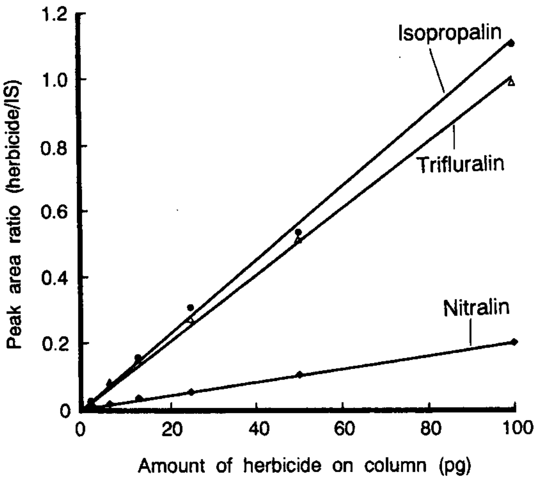

Fig. 8. Calibration curves by SIM in the NICI mode for isopropalin (●), nitralin (◆) and trifluralin (△). They were measured against pendimethalin (500 pg on column) as internal standard (IS). The vertical axis shows the peak area ratio of herbicide to IS. Each point represents the mean of duplicate determinations.

Discussion

The analyses of dinitroaniline herbicides are being made by ultraviolet spectrophotometry [3], thin layer chromatography [4, 5], GC with flame ionization detection [3, 6, 7], GC with nitrogen phosphorus detection [7, 8], GC with electron-capture detection [7—10], high performance liquid chromatography [5], liquid chromatography/MS with NICI [11] and GC/MS with PIEI or NICI [9, 10, 12]. Very recently, the herbicides have been measured by GC with surface ionization detection [7]. In this paper, we have presented PIEI, PICI and NICI mass spectra of seven dinitroaniline herbicides. To our knowledge, such systematic studies in the three modes have not been reported before.

Screening of poisons or drugs is important in forensic science practice. Peaks at m/z 43 and/or 55 (or 57) in the PIEI mode, and those at m/z 19 (F), 29, 41 and/or 57 (or 55) in the PICI mode, can be a good indication for the possibility of the presence of dinitroaniline herbicides.

The NICI mode MS is most powerful for detecting halogen or nitro groups in a chemical [13]. In this study, each of the seven dinitroaniline herbicides has two nitro groups at the aromatic ring; benfluralin, ethalfluralin, profluralin and trifluralin have also trifluoromethyl groups in their structures. All compounds gave intense M^- peaks and constituted base peaks; in addition no fragment peaks appeared except that of M − NO in all mass spectra, showing very high sensitivity of the molecular ion in the NICI mode (Figs. 1−7). The calibration curves by SIM for isopropalin, nitralin and trifluralin, showed very low detection limits as low as 2−20 pg on column (Fig. 8).

In conclusion, the present study shows that the fragment ions in low mass ranges in the PIEI and PICI modes are useful for screening test for the dinitroaniline herbicides. The intense quasi-molecular cations in the PICI mode and the molecular anions in the NICI mode, are useful for estimation of molecular weights. The SIM in the NICI mode is especially powerful for sensitive detection of the herbicides.

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