Identification of Organochlorine Pesticides in Crude Extracts by Mass Spectrometry[1,2]

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Abstract

A method is described for identifying a chlorinated pesticide in crude extracts (i) at 1 ppm by low resolution mass spectrometry with the aid of a recently developed temperature controlled probe and (ii) at 0.01 ppm by high resolution techniques using a photoplate record to determine the mass deficient ions containing chlorine.

This analytical method is feasible wherever ions of the same elemental composition as those derived from an unknown are not otherwise present in the crude extract mass spectrum.

Introduction

The use of mass spectrometry for the identification of pesticides has been suggested in recent years and its advantages for residue analysis adequately discussed (1-6 and references cited therein). The combination of GLC with mass spectrometry was found particularly useful (7-9). Because of the sensitivity of mass spectrometry and its ability to unambiguously identify ions derived from specific compounds, its use for the detection of pesticides in crude extracts has been suggested (1). Time consuming clean-up and separation steps would thus be avoided and loss or chemical change of the residue prevented.

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Organochlorine pesticides are particularly suited for this approach; they lead to unique ions because interfering natural organochlorine compounds are not usually found in commercially important plants (10, 11). The presence of chlorinated pesticides in crude plant extracts is recognizable, therefore, depending on concentration, by either (i) the characteristic peak pattern due to the chlorine isotopes ^{35}Cl and ^{37}Cl or (ii) identification of ions which contain chlorine from high resolution data.

Chlorinated aromatic compounds usually give simple spectra with few and abundant fragment ions (1-5, 12, 13). A compound of this type, the fungicide 2,6-dichloro-4-nitroaniline (DCNA) was chosen for this investigation.

Experimental

2,6-Dichloro-4-nitroaniline

A recrystallized sample (benzene/hexane) of commercially available material (Aldrich Chemical Co.) was used in all experiments.

Extraction Procedure

The procedure was similar to that of Kilgore et al. (14) except that hexane was used as solvent for extraction (cf. 15).

In separate experiments, 1 mg, 100 µg, 10 µg or 1 µg of 2,6-dichloro-4-nitroaniline was added to 100 g of canned peaches cut into small pieces. The peaches were then extracted with hexane (300 ml) with vigorous shaking for 1-1/2 hours. The hexane layer was separated, dried with Na_2SO_4 and the solvent removed. The oily residue was heated at 70°C/0.5 Torr for 30 minutes to remove the more volatile materials. A sample (≃20 µg) was transferred into a capillary tube for direct-introduction to the mass spectrometer ion source.

Mass Spectrometry

The 70-volt mass spectra were obtained with a Bell and Howell/C.E.C. model 21-110B mass spectrometer. The samples were introduced directly into the source using a probe which allowed the

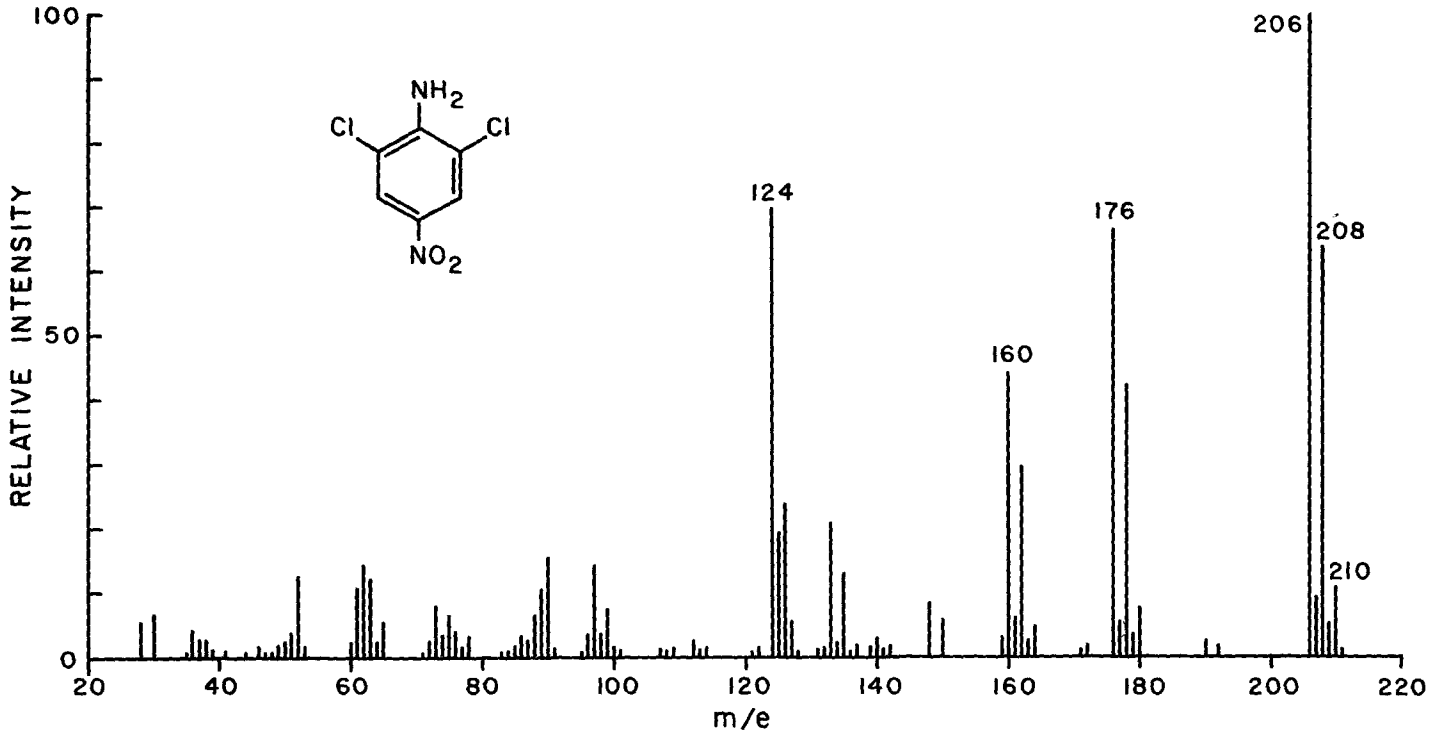

FIGURE 1. MASS SPECTRUM OF 2,6-DICHLORO-4-NITROANILINE.

IONIZATION CHAMBER TEMPERATURE: 150 °C.

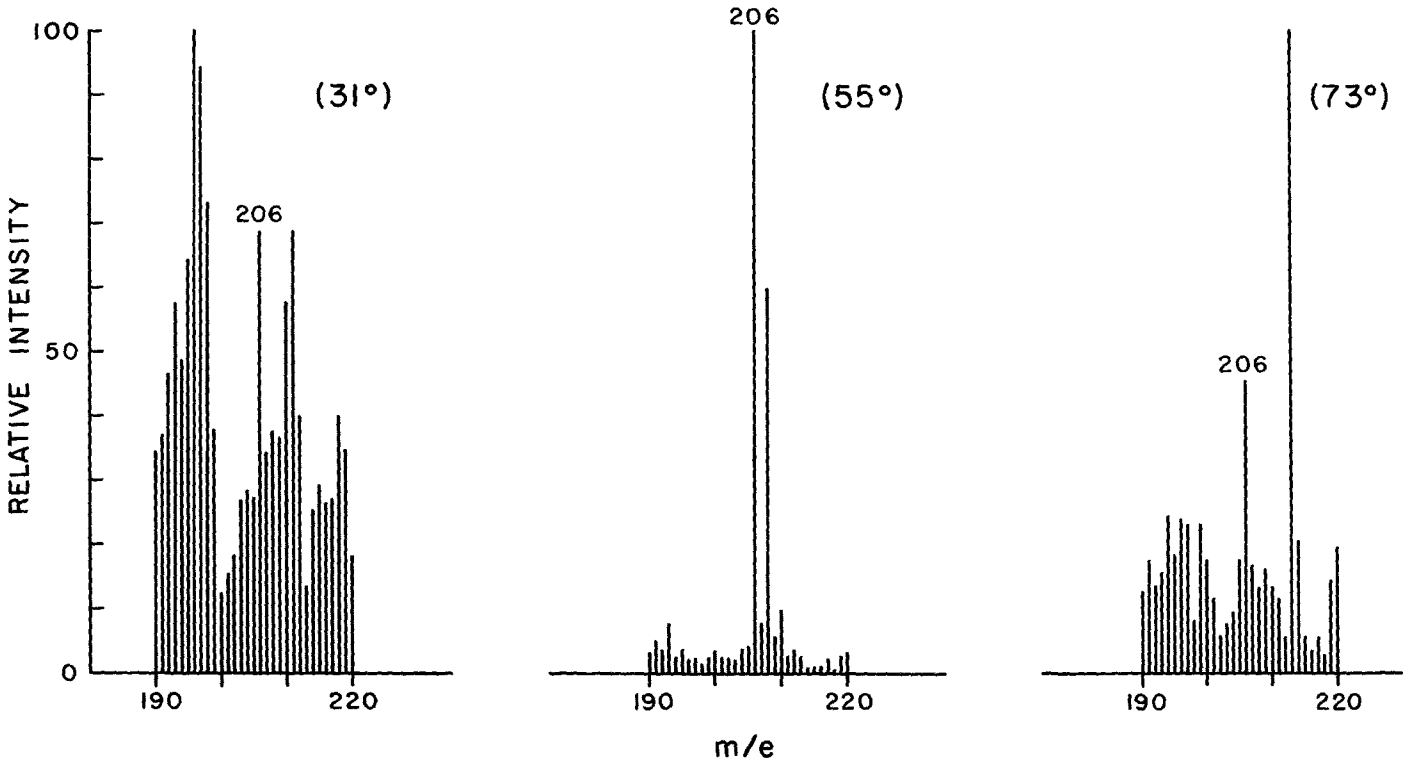

FIGURE 2. PARTIAL MASS SPECTRA, AT SAMPLE TEMPERATURES INDICATED, FOR PEACH EXTRACT CONTAINING 1 PPM 2,6-DICHLORO-4-NITROANILINE. IONIZATION CHAMBER TEMPERATURE: 180 °C.

temperature of the sample to be controlled independently from source temperatures (16). The extracts were introduced at -20°C and slowly heated until operating conditions were optimal. High resolution spectra were recorded on photoplates (Ilford Q2) with a total ion current of about 1×10^{-12} amp. With the lowest concentration of I (0.01 ppm) the photoplate was exposed for 30 minutes while the temperature was raised from 25°C to 60°C. Perfluorokerosene (PFK) was used as an internal mass standard.

Results

Detection of I at 1 ppm by Low Resolution

The spectrum of I is shown in Figure 1. Ions which can be used for diagnostic purposes are the base peak at m/e 206 due to the molecular ion, ^{37}Cl isotope peaks at m/e 208 and 210, and abundant ions at m/e 176, 160 and 124.

Partial mass spectra (from m/e 190 to 200) of a crude peach extract with 1 ppm of I are shown, for different sample temperatures, in Figure 2. The sample fractionated as the temperature was increased until, at about 55°C, the partial pressure of I was greatest and its presence could be clearly recognized from the spectrum. For concentrations of I > 1 ppm the temperature was less critical whereas for concentrations < 0.1 ppm the spectrum of I could not be reliably distinguished from spectra due to other components.

Detection of I at 0.01 ppm by High Resolution

High resolution spectra included a line at m/e 205.9650 due to $(C_6H_4N_2O_2{}^{35}Cl_2)^+$. Because of the mass deficiency of the chlorine isotope, the m/e value of this line was less than that of any other ionic species at nominal m/e 206. It was easily distinguished (see Figure 3) both from ions derived from other components of the extract and from the adjacent line at m/e 205.9922 due to the PFK internal standard.

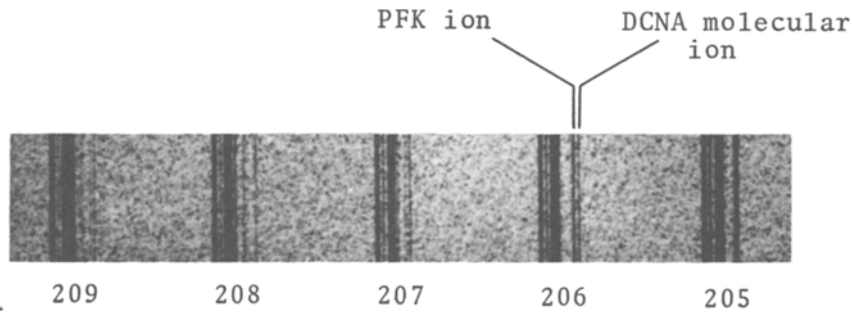

Figure 3. Partial photoplate record of mass spectrum of crude extract containing 0.01 ppm DCNA.

Detection of p,p'-DDT in Carrot Extract

Similar results and detection limits were obtained with p,p'-DDT in crude carrot extract.

Discussion

Mass spectrometry can be used to identify reliably the fungicide 2,6-dichloro-4-nitroaniline (I) in hexane extracts of peaches at levels above 1 ppm (low resolution) or 0.01 ppm (high resolution). With high resolution spectra recorded on photoplates, I can be detected at levels below 0.01 ppm if either the total ion current or the recording time is increased beyond the values cited above.

Mass spectrometric quantitative analysis for I and similar compounds can be based on periodic calibration with samples which contain reference levels of pesticides. Feasible methods include repeated low-resolution scanning or integrating with time a characteristic ion current using either electrical detection (17, 18) or a photographic plate to record the data. Mass spectrometry seems more useful, however, when rapidly screening extracted plant material for low levels of a particular organochlorine compound. The method can be automated. Simultaneous analysis for several pesticides is also feasible if the temperature of the probe is programmed (cf. 19) and/or mass spectral data is processed automatically (2). Data processing is needed where mixtures of organochlorine compounds give rise to complex spectra (20, 21) under electron

impact. Field ionization techniques, however, yield much simpler spectra (22).

For optimum identification of pesticide residues in crude extracts by mass spectrometry: (i) the solvent should extract as much of the pesticide and as little of the plant material as possible; (ii) the molecular ion or a characteristic fragment ion should be abundant in the mass spectrum; (iii) the residues should contain elements not commonly present in plant material (e.g. halogens) — for detection by low resolution mass spectrometry the presence of an element with characteristic isotope distribution (e.g. Cl, Br, S) is important; (iv) fragmentation patterns for all pesticides and metabolites present should be known.

The method described in this paper should be considered as a limiting or extreme approach. Considerable improvement in sensitivity, accuracy and versatility should result from some sample clean-up before mass spectrometry.

Acknowledgments

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References

1. J. JÖRG, M. SPITELLER-FRIEDMANN and G. SPITELLER, Pflanzenschutz-Berichte, Sonderheft, 157 (1967).

2. R. E. LOVINS, J. Agr. Food Chem. 17, 663 (1969).

3. P. ZINK, Arch. Toxikol. 25, 1 (1969).

4. R. O. MUMMA, 157th Meeting of the American Chemical Society, 1969; Division of Agricultural and Food Chemistry, Abstract No. 22.

5. J. A. SPHON and J. N. DAMICO, Org. Mass Spectrom. 3, 51 (1970).

6. J. A. ROSS and B. G. TWEEDY, Org. Mass Spectrom. 3, 219 (1970).

7. L. BERGSTEDT and G. WIDMARK, Chromatographia 3, 59 (1970).

8. F. J. BIROS, Anal. Chem. 42, 537 (1970).

9. F. J. BIROS and A. C. WALKER, J. Agr. Food Chem. 18, 425 (1970).

10. L. FOWDEN, Proc. Roy. Soc. B, 171, 5 (1968).

11. J. W. HYLIN, R. SPENGER and F. A. GUNTHER, Residue Rev. 26, 127 (1969).

12. J. JÖRG, R. HOURIET and G. SPITELLER, Monatsh. Chem. 97, 1064 (1966).

13. O. HUTZINGER, W. D. JAMIESON and S. SAFE, In preparation.

14. W. W. KILGORE, in "Botran Symposium", The Upjohn Co., Kalamazoo, Michigan, 1965.

15. W. F. EDMUNDSON, J. J. FREAL and J. E. DAVIES, Environmental Research, 1, 240 (1967).

16. W. D. JAMIESON and F. G. MASON, Rev. Sci. Instr. 41, 778 (1970).

17. J. R. MAJER and A. A. BOULTON, Nature, 225, 658 (1970).

18. A. A. BOULTON and J. R. MAJER, J. Chromatog. 48, 322 (1970).

19. O. HUTZINGER, W. D. JAMIESON and V. ZITKO, Nature 226, 664 (1970).

20. H. D. SCHARF and G. METZINGER, Tetrahedron, 23, 3067 (1967).

21. J. N. DAMICO, R. P. BARRON and J. M. RUTH, Org. Mass Spectrom. 1, 331 (1968).

22. J. N. DAMICO, R. P. BARRON and J. A. SPHON, J. Mass Spectrometry and Ion Physics 2, 161 (1969).