Mass Spectral Pattern of Mirex (dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta [*cd*] pentalene) and of Kepone (decachlorooctahydro-1,3,4-metheno-2H-cyclobuta [*cd*]-pentalen-2-one) and its Application in Residue Analysis[1,2]

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Introduction

Gas chromatography is usually the method of choice for the analysis of pesticide residues because of its wide applicability and high sensitivity. Confirmatory evidence is required, however, where the sample history is unknown. The ubiquitous polychlorinated biphenyls (PCB's) give gas chromatographic peaks which elute close to or coincident with many chlorinated pesticides and constitute a question as to the absolute authenticity of glc data describing residue levels in the environment. The problem of interference of PCB's in glc analysis of DDT is well documented (1,3,5).

Mirex is characteristically a late elutant from the glc column and is easily distinguished from other chlorinated insecticides. Despite its unique property, Mirex can be confused with some of the peaks of PCB's. The two PCB's studied in our laboratory, Aroclor 1254 and Aroclor 1260[3] have late eluting peaks that overlap with that of Mirex when analyzed on a 6-ft, U-shape column packed with either 3% QF-1 or 3% OV-210.

The use of mass spectrometry for positive identification of pesticide residues has been suggested (3,6). The data reported here are a preliminary description of the application of mass spectrometry for residue identification with these two insecticides.

Experimental

A Bell-Howell model 21-490 mass spectrometer was

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[2] Correspondence should be addressed to CMH

Table 1. Intensities of chlorine isotope peaks relative to the parent peaks (values are in % of parent peaks)

Cl present / no. of ^{37}Cl	1	2	3	4	5	6	7	8	9	10	11	12
peak	P+2	P+4	P+6	P+8	P+10	P+12	P+14	P+16	P+18	P+20	P+22	P+24
Cl *	32.6											
Cl_2*	65.3	10.6										
Cl_3*	99.8	31.9	3.47									
Cl_4*	131.0	63.9	14.0	1.15								
Cl_5*	163.0	106.0	34.7	5.66	0.37							
Cl_6*	196.0	161.0	69.4	17.0	2.23	0.11						
Cl_7*	221.43	221.95	120.23	39.02	7.55	0.86	-					
Cl_8*	260.95	297.99	194.44	79.33	20.66	3.34	0.28	-				
Cl_9	293.52	382.86	291.49	162.94	53.17	10.15	1.39	0.10	-			
Cl_{10}	326.10	478.78	416.66	237.71	93.09	25.25	4.71	0.50	0.33	-		
Cl_{11}	358.70	585.04	572.54	373.43	170.53	55.58	12.94	2.00	0.18	-	-	
Cl_{12}	391.98	703.85	785.28	581.42	293.17	111.57	30.86	5.93	0.60	0.06	-	-

*Values taken from Silverstein and Bassler (7) after the calculations by Beynon (1).

used. The sample, contained in a glass capillary tube, was introduced directly into the ionization source using a probe heated independently of the source. In order to obtain optimum operating conditions, the probe was heated to 140-150°C. Mass spectra were taken at ionization energies of 10 and 80 electron volts.

Results and Discussion

Mirex and Kepone have well-defined and characteristic peak patterns in their mass spectra which include the parent peak. Because of the numbers of chlorine atoms involved, the parent peak and each fragment peak are readily recognized due to the ^{35}Cl and ^{37}Cl isotope ratios. The isotopic abundance ratios of compounds containing up to 8 chlorine (1,7) and up to 10 chlorine atoms (8) have been calculated. We have expanded the calculation to 12 Cl following the probability formula used by Beynon (1):

$$^{w}C_{r} \left(\frac{a}{100}\right)^{r} \left(\frac{100-a}{100}\right)^{wr}$$

where a = % natural abundance of ^{37}Cl (24.6%),
w = total number of Cl atoms in the molecule,
r = number of ^{37}Cl atoms in the molecule.

The effects of ^{13}C isotope can be ignored due to its relatively low natural abundance (1.069%) as compared to ^{37}Cl. Table 1 shows the ion intensities of chlorine isotope peaks. Values up to 8 Cl are those of Beynon (1) presented here as per cent of the parent peak (7).

While the final mass presentation of a quadrupole mass spectometer is linear, that of a magnetic mass spectrometer is logarithmic which makes the peak identification rather tedious and difficult. The chlorine isotope ratios greatly facilitate this task, particularly in the identification of molecular and fragment ions of m/e > 300.

The mass spectra and results of mass measurement are presented in Figures 1-4. In this study we found that it was rather difficult to distinguish the true peaks from the background at m/e < 100. Therefore, only the peaks above m/e 100 are illustrated. Both Mirex

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[3] Monsanto Company, St. Louis, Missouri.

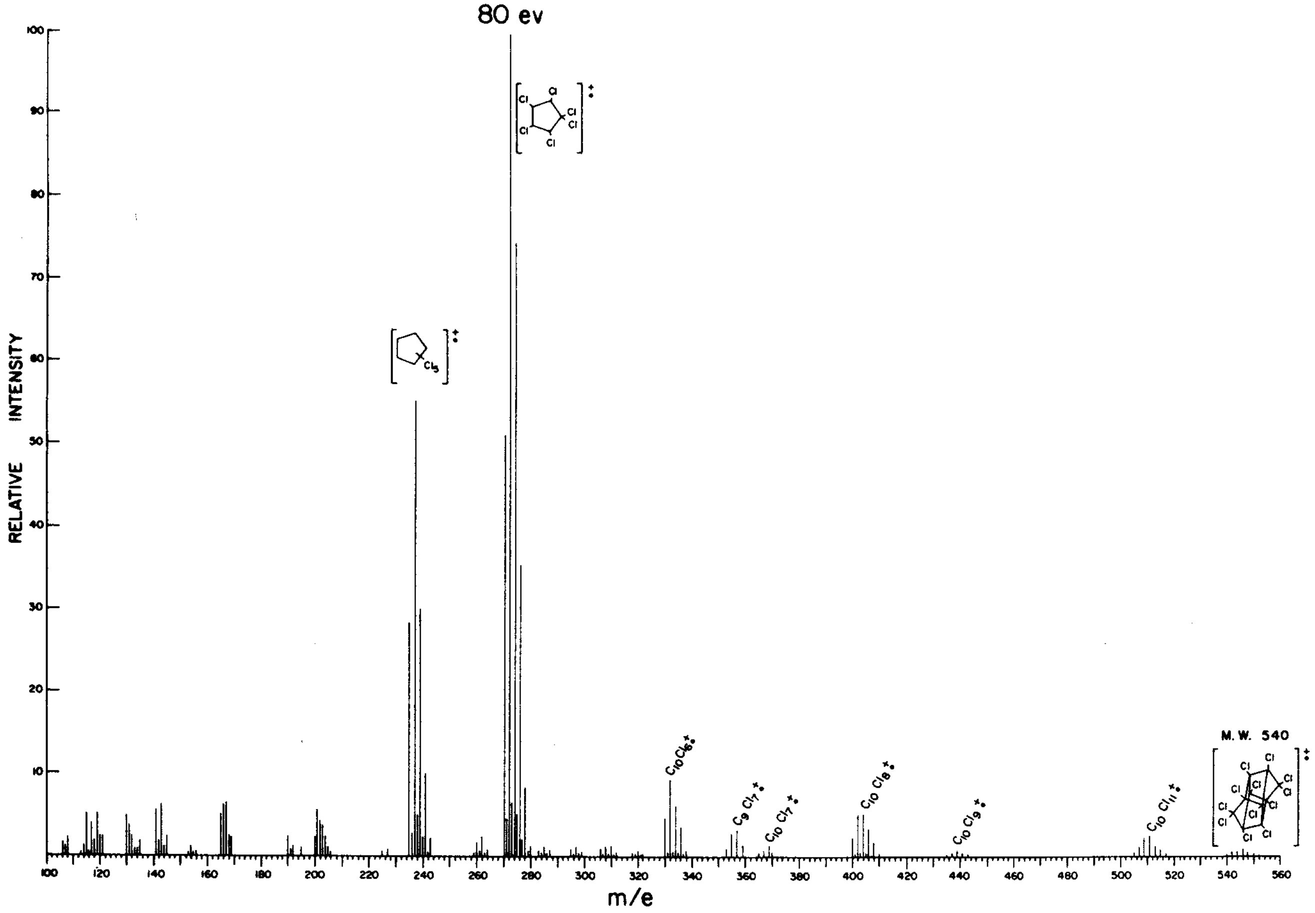


Figure 1. Mass spectrum of Mirex at ionization energy of 80 ev.

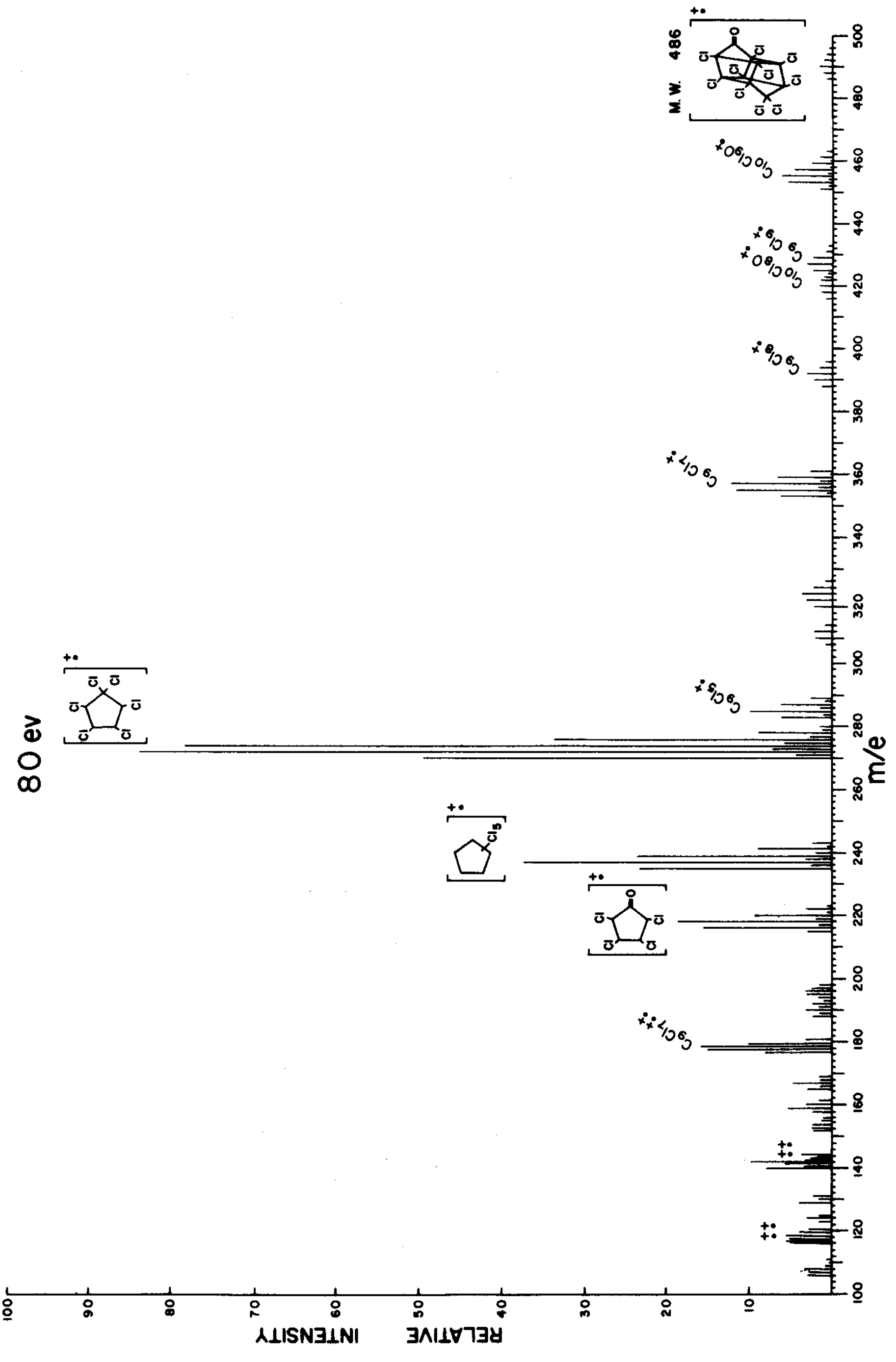
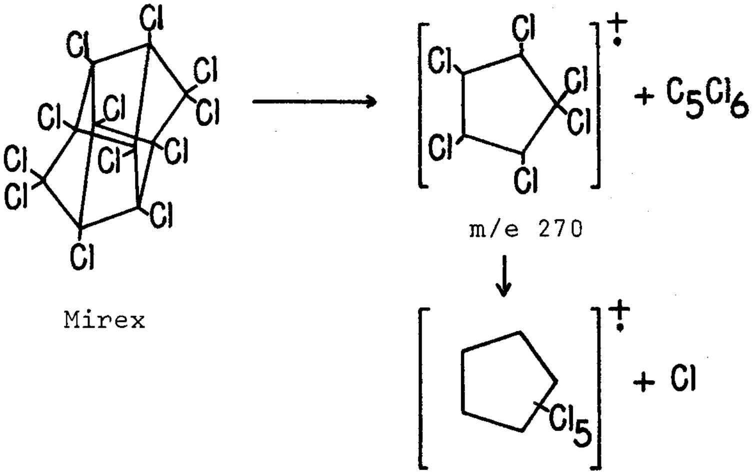
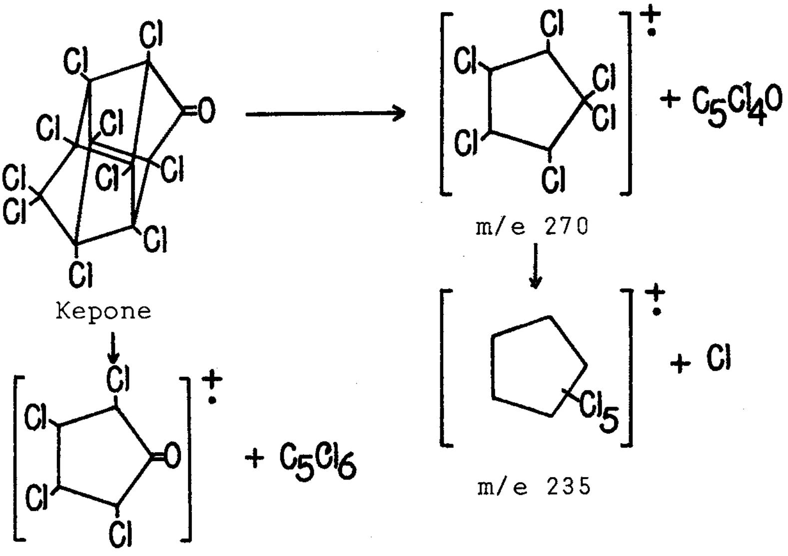


Figure 2. Mass spectrum of Kepone at ionization energy of 80 ev.

and Kepone yield strong peaks at m/e 270 corresponding to the positively charged hexachloro-cyclopentadiene. This suggests the retro-synthesis type of fragmentation similarly observed among the chlorinated cyclodiene pesticides (4). The second strong peak at m/e 235 is undoubtedly derived from the loss of a chlorine from fragment 270.





The presence of 19.60% of $C_5Cl_4O^{\dot{+}}$ at m/e 216 with respect to the base peak (m/e 270) in the Kepone spectrum shows that the charge is alternately localized in both halves of the molecule. This assumption can be extended to Mirex. Other ions of much lesser intensities, therefore of negligible importance from the residue viewpoint, appear to

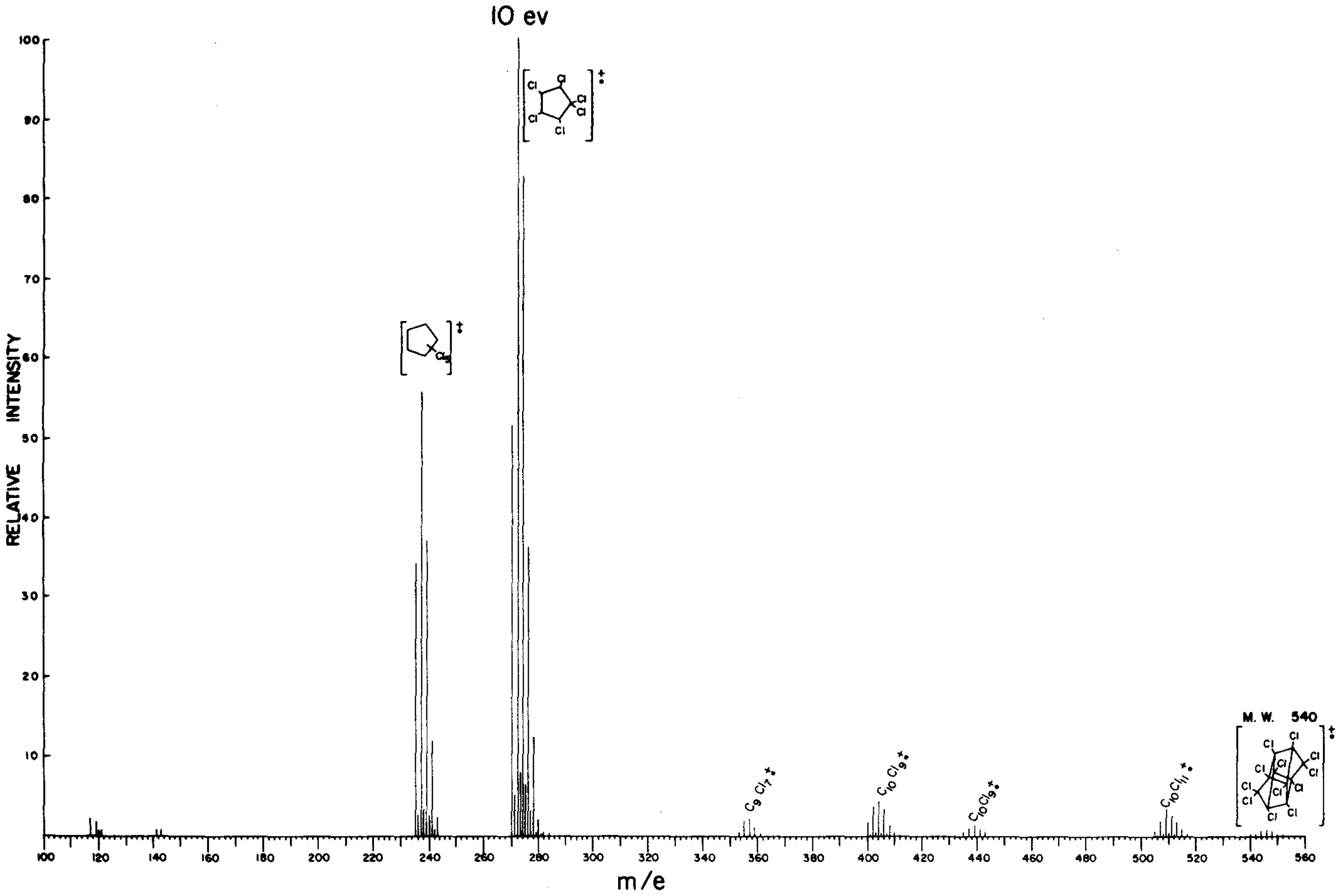


Figure 3. Mass spectrum of Mirex at ionization energy of 10 ev.

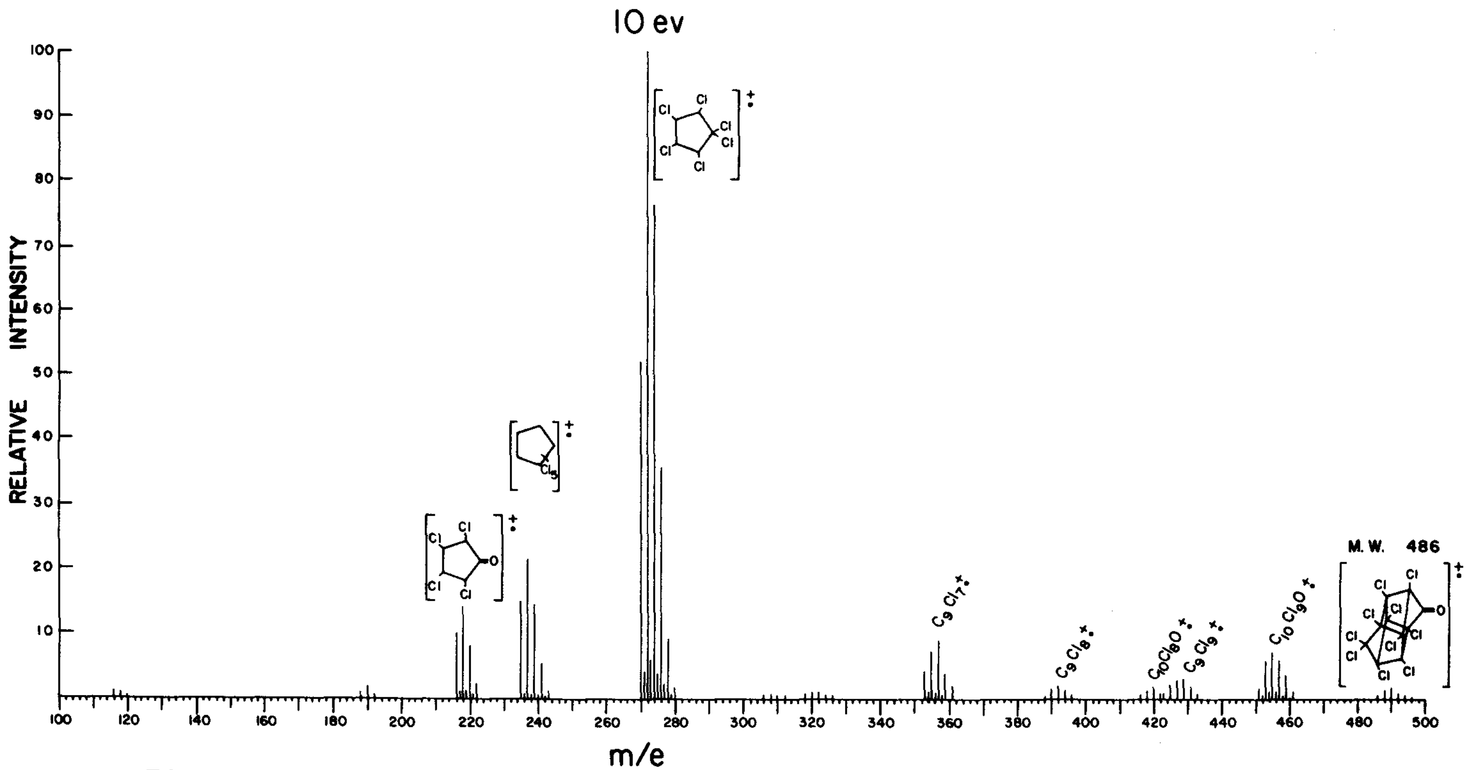


Figure 4. Mass spectrum of Kepone at ionization energy of 10 ev.

result mainly from successive losses of Cl in Mirex. Kepone exhibits, in addition, the ease of ring rupture at the ketone position with probable subsequent losses of Cl. Other minor peaks, particularly at m/e < 235, may be resulted from a complex of secondary decomposition and/or recombination processes. The metastable ions could not be detected under the conditions of our experiments; thus no attempt was made to identify either the minor peaks or the multiplets.

When the electron energy is lowered to 10 eV, most of the minor peaks disappear (Figs. 3 and 4). The parent, the m/e 270, and the m/e 235 peaks remain. This makes the use of mass spectra in residue identification of Mirex and Kepone easier because of minimal interference.

We suggest the use of the clusters of isotope peaks at m/e 270 and m/e 235, and the molecular ions (m/e 540 for Mirex and m/e 486 for Kepone) as characteristics for identification. Kepone requires, in addition, the isotope clusters at m/e 216. The m/e 270 and m/e 235 fragments are not free from interference. The chlordane and heptachlor series of insecticides produce these two groups of ions (4). Nevertheless, their parent molecular ions are clear from overlapping with any fragment of Mirex or Kepone; chlordane, m/e 406; nonachlor, m/e 440; chlordene, m/e 336; heptachlor, m/e 370; heptachlor epoxide, m/e 386.

Acknowledgments

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References

1. Beynon, J. H. Mass Spectometry and its Applications to Organic Chemistry, p 294 (1960), Elsevier, New York
2. Biros, F. J., Walker, A. C., and Medbery, A. Bull. Environ. Contam. Toxicol. 5,317 (1970)
3. Bonelli, E. J. Amer. Lab. 3(2),27 (1971)
4. Damico, J. N., and Barron, R. P. Organ. Mass Spectrom. 1,331 (1968)
5. Gustafson, C. G. Environ. Sci. Tech. 4,814 (1970)
6. Hutzinger, O., and Jamieson, W. D. Bull. Environ. Contam. Toxicol. 5,587 (1971)
7. Silverstein, R. M., and Bassler, G. C. Spectrometric Identification of Organic Compounds, p 29 (1967), John Wiley & Sons, New York
8. Smithson, L. D., Bhattacharya, A. K., and Hedberg, F. L. Organ. Mass Spectrom. 4,383 (1970)