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# Isolation and Characterization of the Herbicide Dimethyl Tetrachloroterephthalate by Gas Chromatograph-Mass Spectrometer-computer Techniques

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The analysis of pesticides and pollutants in environmental samples has rapidly gained importance in recent years due to the toxicity and potentially hazardous nature of many of these compounds and their metabolites. Newer and more sophisticated analytical techniques are continually being developed to monitor these compounds, and significant advances in methodology have been made in the last decade. One of the most versatile and important analytical tools currently being used for the analysis of pesticides and pollutants is the Gas Chromatograph-Mass Spectrometer - Computer (GC-MS-Com) (BIROS 1971)(OSWALD et al. 1974). This instrument, when used in both the electron impact and chemical ionization modes, provides the required sensitivity and specificity that is desirable of any modern analytical technique (VANDER VELDE et al. 1975).

During a current research study of organophosphate pesticides in water samples from the Imperial Valley in California, an unknown component appeared as a peak in the gas chromatograms of several samples. This compound was identified by GC-MS as dimethyl tetrachloroterephthalate also known as DCPA or Dacthal (WISSWESSER 1976). DCPA is used extensively as a pre-emergent herbicide on onion, cabbage, and cotton crops. Approximately 100,000 lb per year of this herbicide are used over a section of the Imperial Valley in California, (ECCLES 1976) and it apparently finds its way into irrigation runoff water and eventually into streams and lakes.

Current methods for the determination of DCPA in environmental samples involve electron capture gas liquid chromatography (TESSARI 1971, WIERSMA 1969) and infrared (WAPENSKY 1969). Although one report (MILLER et al. 1974) describes the use of GC-MS for the detection of DCPA residues in environmental samples, no data were published on the mass spectrum of this compound. A Chemical Abstract and Pollution Index computerized search revealed no prior publication of the mass spectrum of DCPA. A computerized library search

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of the Mass Spectral Search System (MSSS) data bank (HELLER et al. 1975) did not produce any positive matches.

The purpose of this report is to describe the isolation and characterization of DCPA in water samples by GC-MS.

## METHODS AND MATERIALS

Isolation of DCPA From Water. 900 mL of the sample were extracted with dichloromethane (3 X 100 mL). The combined extract was dried for 2 h over sodium sulfate, then filtered through glass wool into a Kuderna-Danish apparatus and concentrated to 1.0 mL. The extract was then concentrated to dryness under a stream of $N_2$ and redissolved in 0.5 mL of hexane. Five microliters of this solution were injected into the gas chromatograph for preliminary screening purposes.

Equipment. A Tracor Model 550[1] gas chromatograph equipped with a Ni-63 detector was used for retention time studies. Samples were chromatographed isothermally at 180°C on 1.8 m X 4 mm ID glass columns packed with either 3% OV-101 on 100/120 mesh Gas Chrom Q or 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport. $Ar/CH_4$:95/5, v/v was used as carrier gas at a flow rate of 60 mL/min.

GS-MS analyses were performed on a Finnigan Model 4010 GC-MS-Data System[1]. The GC column was packed with 3% OV-101 on 100-120 mesh Gas Chrom Q. Helium at a flow rate of 30 mL/min was used as carrier gas. A μl aliquot of the concentrated hexane extract was injected into the gas chromatograph (oven temperature 170°C, isothermal). Data acquisition was commenced 1 min after injection. The mass spectrometer was operated using an ionizing voltage of 70 eV and an ionizing current of 250 μA.

## RESULTS AND DISCUSSION

Table 1 lists relative retention time data for DCPA in a water sample and DCPA standard. The retention times are relative to aldrin.

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[1] The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

TABLE 1.--Relative Retention Time of DCPA Relative to that of Aldrin.

| DCPA | SP2250/SP2401 | OV-101 |
|---|---|---|
| sample | 0.863 | 1.009 |
| standard | 0.865 | 1.006 |

A standard injection of DCPA determined the concentration of this herbicide in the water sample to be less than 1 µg/L.

Figure 1 shows the total ion chromatogram of a contaminated water sample extract. The chromatogram in Fig. 1 shows two major peaks, (A) and (B). GC-MS analysis identified peak (A) as malathion, and peak (B) as DCPA. Confirmation of identity spectrum and relative retention time with that of an authentic standard of DCPA analyzed under identical conditions.

Figure 2 shows the mass spectrum of compound (B) in a contaminated water sample extract, and the mass spectrum of an authentic sample of DCPA.

The mass spectrum of DCPA displays a typical 4 chlorine isotope cluster at the molecular ion $M^+$ 330 (4 Cl). Major fission products result from loss of methoxyl ($M - OCH_3$) to give an intense 4 chlorine isotope cluster at m/e 299, followed by ejection of CO to give a 4 chlorine isotope cluster at m/e 271. The isotope cluster at m/e 271 could also be generated by loss of a carbomethoxyl group ($COOCH_3$) from the molecular ion. The ion at m/e 271 could conceivably lose a $CH_3$ group to give a 4 chlorine isotope cluster at m/e 256, followed by loss of Cl to give a 3 Cl isotope cluster at m/e 221, from which in turn, is expelled $CO_2$ resulting in a 3 Cl isotope cluster at m/e 177. The ion at m/e 177 could then lose Cl to give a 2 chlorine isotope cluster at m/e 142 which in turn loses Cl to give a 1 Cl isotope cluster at m/e 107.

The metabolic fate and degradation of DCPA in soils and aquatic systems need further investigation. It is in this area that GC-MS-systems will play an important role.

## ACKNOWLEDGEMENT

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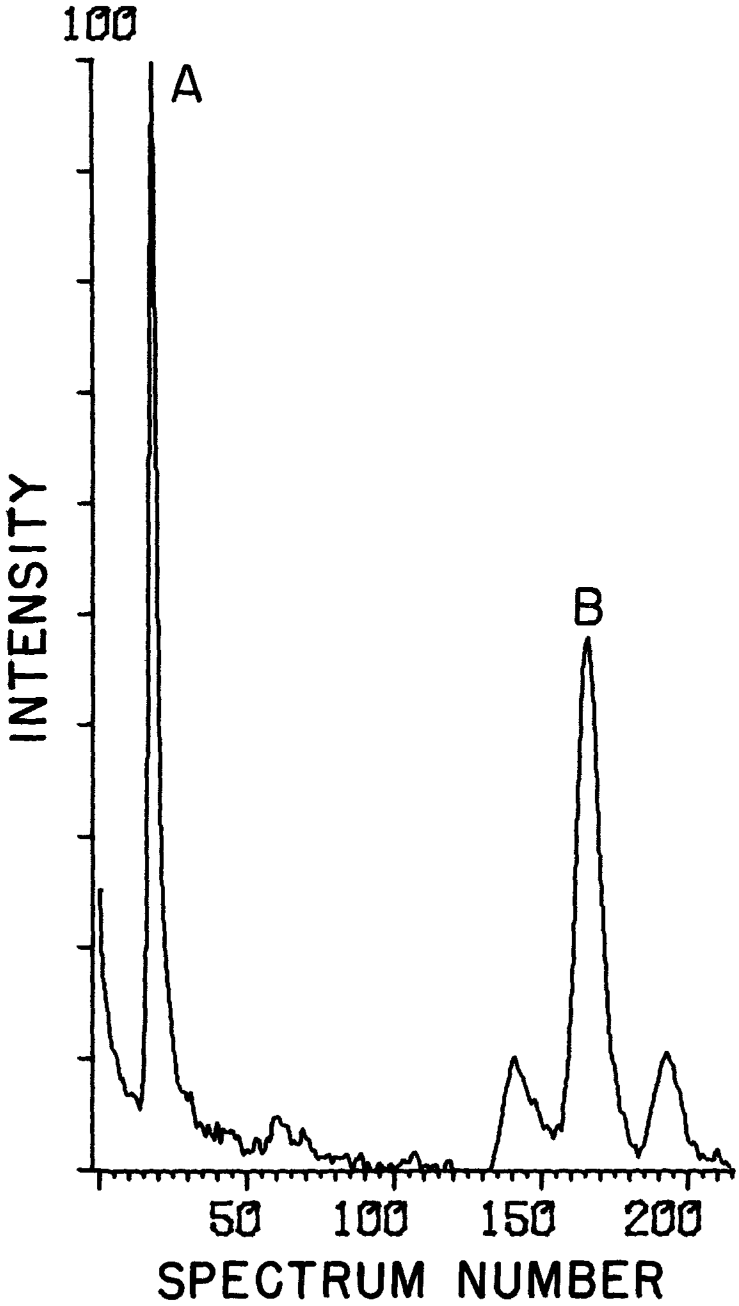

Figure 1. Total ion chromatogram of contaminated water sample extract. A) Malathion, B) DCPA.

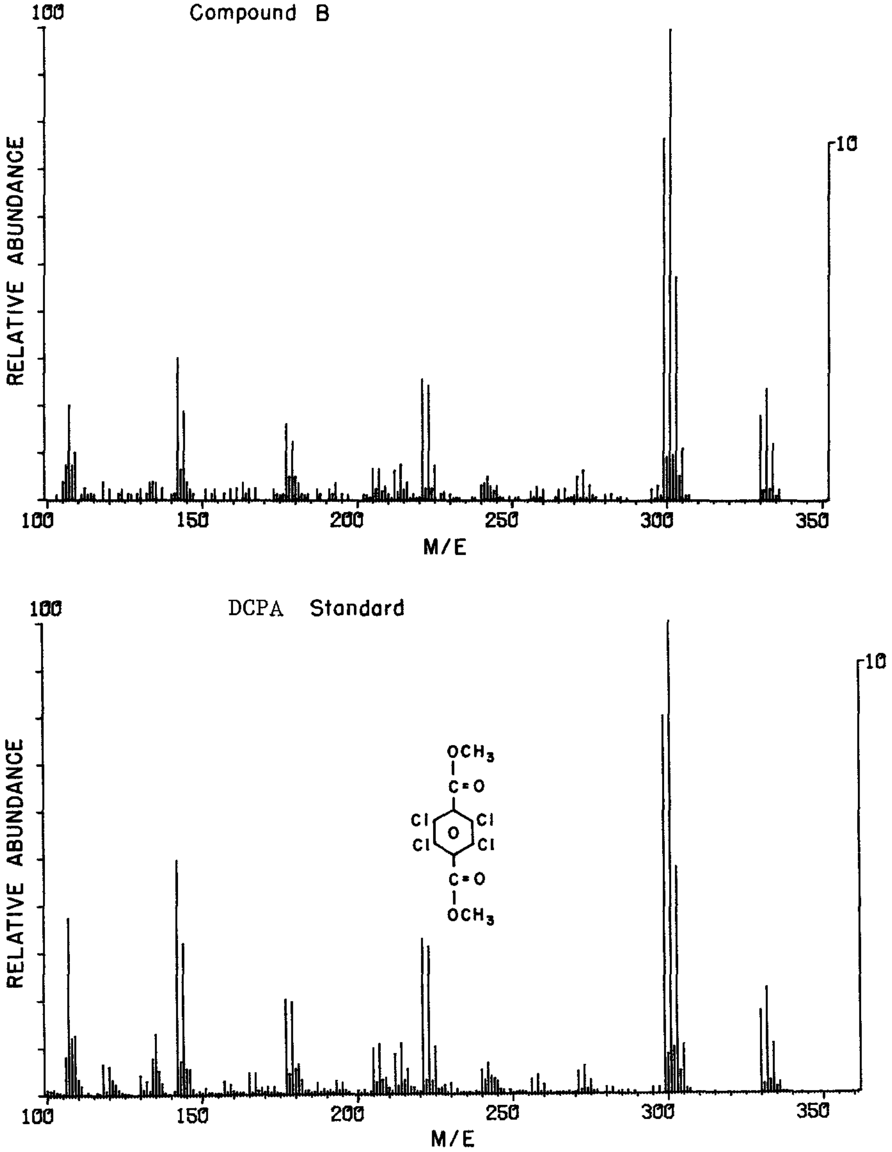

Figure 2. Mass spectra of compound B in contaminated water extract, and DCPA standard.

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