Field Desorption Mass Spectrometry of Standard Organophosphorus Pesticides and Their Identification in Waste Water

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The characteristic behaviour of four groups of commonly used organophosphorus pesticides such as phosphates, phosphorothionates, phosphorothiolates and phosphorodithioates has been investigated by field desorption mass spectrometry. Their spectra show molecular ions of high abundance and characteristic fragmentation patterns. The phosphates and phosphorothionates usually show the α-cleavage with respect to the P-atom with and without proton transfer. In contrast, the phosphorothiolates and phosphorodithioates usually show the β-cleavage from the P-atom. The fragments with the charge retention on the phosphorus moiety were also observed in the field desorption mass spectra, although their abundances were often relatively low.

The analyses of standard mixtures as well as some waste water samples indicate that field desorption mass spectrometry is suitable for the identification of organophosphorus pesticides at nanogram level in mixtures and environmental samples without preliminary separation and purification.

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INTRODUCTION

Trace analyses of biocides encountered in environmental studies are particularly difficult because often their concentrations are low and the mixtures obtained from biological samples are almost always very complex. Thus, in order to achieve reliable data, analytical methods with sufficient selectivity and sensitivity are required.

In the past decade, a vast number of analytical methods have been developed to solve the environmental problems. Among these methods mass spectrometry (MS) combined with gas chromatography or liquid chromatography together with efficient data acquisition and processing is the most important and useful tool. The advantages it offers are high selectivity and sensitivity as well as supply of exact molecular weight and structural information. Therefore, mass spectrometric techniques are widely used in qualitative and quantitative analyses of environmental chemicals.

In recent years, organophosphorus pesticides have found increasing use in many aspects of pest control, and in many countries the replacement of organochlorine insecticides is now almost completed. The use of the electron impact (EI) MS in the investigation of the organophosphorus pesticides has been reviewed in the monography by Safe and Hutzinger[1] and individual publications.[2−6] However, EI mass spectra may contain high fragment peaks and often result in small or undetectable molecular ions. On the other hand, field ionization (FI) MS[7,8] and chemical ionization (CI) MS[9,10] have been recommended to minimize the fragmentation of the compounds so as to give high intensity of the molecular ion, $(M)^{+\cdot}$ or the protonated molecule, $(M+H)^+$. One essential limitation is, however, that the substances studied by the methods described above must be volatile and should not decompose upon evaporization in vacuum. In order to overcome this difficulty in environmental analyses, field desorption (FD) MS has been introduced.[11,12] The FD technique is suitable for the investigation of a wide variety of organic substances without vaporization, in particular, for the detection, identification and determination of underivatized, polar substances.[13,14] It could be expected, therefore, that very small amounts in the order of submicrograms of biocides such as organophosphorus pesticides, their metabolites and degradation products present in complex mixtures could be analyzed successfully. The utility of low and high resolution FD-MS in the investigation of organochlorine, phenylurea, carbamate and thiocarbamate pesticides has been demonstrated previously by Schulten et al.,[15−17] by Fales et al.[18] and by Yamato et al.[19,20].

The present article can be divided into three parts: First, the recording and interpretation of the FD mass spectra of a number of important

organophosphorus pesticides; second, the analysis of model mixtures consisting of several pesticide standards by FD-MS; and third, the identification of the parent organophosphorus pesticides and/or degradation products in crude extracts of samples of Chinese river water.

EXPERIMENTAL

Materials

The standard organophosphorus pesticides such as dimethoate and trichlorphon (98%) were obtained from the Institute of Environmental Chemistry, Academia Sinica, China, the other standards (93–99%) employed in our studies were purchased from Polyscience Corporation, Niles, Illinois 6048, USA. Stock solution of these substances adjusted to ca. 100 ppm were prepared by dissolving the pure substances in methanol, acetone or distilled water, depending on their solubilities.

Two liters of water samples from the Liang Shui river close to Peking were extracted with chloroform (2 × 10 ml) in a separatory funnel. Extracts were dehydrated by anhydrous sodium sulfate, then filtered and reduced to 1 ml using a concentrator with a water bath maintained at 35–40°C.

Field desorption mass spectrometry

The FD mass spectra were recorded on a home-built single focusing mass spectrometer with mono-FD ion source[14] and, for control, repeated on a commercial Varian MAT-731 double-focusing mass spectrometer with a combined EI/FD source. The spectra of most standards were examined at a resolution between 1000 and 2000 (10% valley) using electrical detection.

The high-temperature activated emitters employed in all experiments were 10 μm diameter tungsten wires on which carbon microneedles of 30–70 μm in length were grown under benzonitrile atmosphere.[21] For the mass spectrometric identification, about 10–30 μl of the sample solution were loaded on the emitter by means of a microliter syringe under the microscope. After the solvent was evaporated, the emitter coated with solid (or liquid) sample was introduced into the source of the mass spectrometer. The optimal distance between the emitter and the plate cathode was adjusted to 2–3 mm. The ionization efficiency was calibrated on m/z 58 in the field ionization mode by introducing acetone vapour. The accelerating voltages were for the field anode +8 kV and −4 kV for the opposing cathode.

The FD spectra of standards were obtained at the best anode temperature (BAT), and in most cases the characteristic fragmentation pattern additionally was examined above the BAT. In general, during the measurement the emitter heating current was raised linearly from 0 to

TABLE I

Standards of Organophosphorus Pesticides Investigated by FD-MS

Structural Formula:

$$\begin{array}{c} RO \\ \quad\;\; \diagdown \\ \qquad P{=}X_2 \\ \quad\;\; \diagup \quad \diagdown \\ RO \qquad\; X_1{-}Z \end{array}$$

(a) Phosphates and Phosphorothionates

No	Chemical Name	X_1	X_2	R	Z	Mol. Wt.	Synonyms
1	O,O-Dimethyl O-(2,2,-dichlorovinyl) phosphate	O	O	CH_3	$-CH{=}CCl_2$	220	Dichlorvos (DDVP)
2	O,O-Dimethyl O-(2-carbomethoxy-1-methylvinyl)phosphate	O	O	CH_3	$-(CH_3)C{=}CHCO_2CH_3$	224	Phosdrin (Mevinphos)
3	O,O-Dimethyl O-(p-nitrophenyl) phosphorothionate	O	S	CH_3	$-C_6H_4NO_2$	263	Parathion-methyl
4	O,O-Dimethyl O-(4-thiomethyl-3-tolyl)phosphorothionate	O	S	CH_3	[structure]	278	Fenthion
5	O,O-Diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl)phosphate	O	O	C_2H_5	[structure]	288	Diazoxon
6	O,O-Diethyl O-(p-nitrophenyl) phosphorothionate	O	S	C_2H_5	$-C_6H_4NO_2$	291	Parathion-ethyl
7	O,O-Dimethyl O-(4-(methyl sulphinyl)-m-tolyl)phosphorothionate	O	S	CH_3	[structure]	294	Fenthion-O-analog
8	O,O-Diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothionate	O	S	C_2H_5	[structure]	304	Diazinon
9	O,O-Dimethyl O-(2,4,5-trichlorophenyl) phosphorothionate	O	S	CH_3	[structure]	320	Ronnel (Fenchlorphos)

(b) Phosphorothiolates and Phosphorodithioates

No.	Name					Mass	Trivial name
10	O,O-Dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate	S	S	CH_3	$-CH_2CONHCH_3$	229	Dimethoate (Cygon)
11	O,O-Diethyl S-(ethylthiomethyl) phosphorodithioate	S	S	C_2H_5	$-CH_2SC_2H_5$	260	Phorate
12	O,O-Diethyl S-(2-(ethylthio)ethyl) phosphorodithioate	S	S	C_2H_5	$-C_2H_4SC_2H_5$	270	Disulfoton (Di-Syston)
13	O,O-Dimethyl S-(4-oxo-1,2,3-benzotriazin-3(4H)-yl-methyl) phosphorothiolate	S	O	CH_3	[structure]	301	Guthoxon
14	O,O-Dimethyl S-(4-oxo-1,2,3-benzotriazin-3(4H)-yl-methyl) phosphorodithioate	S	S	CH_3	[structure]	317	Guthion (Azinphos-methyl)
15	O,O-Dimethyl S-phthalimidomethyl phosphorodithioate	S	S	CH_3	[structure]	317	Imidan (Phosmet)
16	O,O-Dimethyl S-(1,2-bis(ethoxycarbonyl) ethyl) phosphorodithioate	S	S	C_2H_5	$-CHCO_2C_2H_5$ $CH_2CO_2C_2H_5$	330	Malathion
17	O,O-Diethyl S-(6-chloro-2-oxo-benzoxazolin-3-yl) phosphorodithioate	S	S	C_2H_5	[structure]	367	Zolone (Phosalone)
18	O,O,O',O'-Tetraethyl S,S'-methylene bis-phosphorodithioate	S	S	C_2H_5	$-CH_2SP(OC_2H_5)_2$	384	Ethion
19	S,S'-1,4-Dioxone-2,3,-diyl bis(O,O-diethyl phosphorodithioate)	S	S	C_2H_5	[structure]	456	Dioxathion

c) Other Organophosphorus Pesticides

No.	Name					Mass	Trivial name
20	O,S-Dimethyl phosphoramidothiolate	—	O	CH_3O CH_3S	NH_2	141	Monitor (Methamidophos)
21	O,O-Dimethyl-(2,2,2-trichloro-1-hydroxyethyl) phosphonate	—	O	CH_3	$-CHCCl_3$ OH	256	Trichlorphon

30 mA by a programmable control unit. For the analyses of the waste water extracts, cyclic magnetic scanning was carried out over a mass range between m/z 50 and m/z 500 in which all substances to be identified were included. The signals were electrically recorded, acquired and processed (averaged) with a Varian SS 200 data system. Alternatively, the ion beams of the individual molecular ion groups of the samples examined were accumulated on a multichannel analyzer (NS–570A Tracor Northern, U.S.A.)[22–24] and its data output was performed by an X-Y plotter of type 7004B Hewlett–Packard.

RESULTS AND DISCUSSION

FD mass spectra of standards

Twenty-one standards of organophosphorus pesticides have been investigated by FD-MS. Their structures and molecular weights are shown in Table I. Except for **20** and **21**, they can be divided into four groups: phosphates, phosphorothionates, phosphorothiolates, and phosphorodithioates. The general structure of the common organophosphorus pesticides is shown in Table I, where Z is a moiety which can be aliphatic or aromatic; R is either methyl or ethyl; X_1 and X_2 can be either an oxygen or sulfur atom. The results of FD-MS of the standards are given in Table II.

The FD mass spectra of the four major classes of organophosphorus pesticides possess the following features: First, for all substances, at the BAT, intense currents were recorded for the molecular ion $(M)^{+\cdot}$ or for the protonated molecule $(M+H)^+$, except for the pesticides **1**, **11** and **21** because these standard compounds are too volatile for FD. Most of the substances investigated exhibited the base peak formed by the $(M)^{+\cdot}$ or $(M+H)^+$ ion. When the emitter temperature was raised above the BAT, all the compounds examined displayed fragmentation, but the molecular ion remained the base peak, except for **10**, whose FD spectrum was more complex. Second, in contrast to the fragmentation pattern in the EI spectra, the substances in the FD mass spectra usually do not show rearrangements, but are characterized by direct bond cleavages. This fundamental property of FD has been reported for many classes of compounds which contain hetero-atoms.[14, 25] The fragmentation pattern of the organophosphorus pesticides studied depends generally on the X_1 function and the nature of the Z moiety. In the phosphates and phosphorothionates, the relatively intense fragments are usually produced by the α-cleavage with and without proton transfer to form the ion $(HOZ)^+$ and $(OZ)^{+\cdot}$. In the FD spectra of phosphorothiolates and phosphorodithioates, the intense fragments are generally produced by the

TABLE II

Significant Ions in the FD Mass Spectra of Standards (w = weak, relative abundance < 1 %; vw = very weak, relative abundance < 0.1 %)

a) Phosphates and Phosphorothionates

Compound	$(M)^{+\cdot}$	$(M+1)^+$	$(M+2)^+$	$(HOZ)^+$	$(OZ)^+$	$(M-OZ)$†	Other m/z (%)
1	10	vw	6	55	40	vw	279 (100), 127 (10)
2	4	100	vw	3	—	—	113 (90), 195 (50)
3	100	32	16	vw	—	—	
4	100	46	42	vw	3	3	263 (2)
5	100	52	9	62	—	—	153 (23)
6	100	38	15	w	—	—	263 (6)
7	100	12	6	4	vw	vw	171 (2), 153 (w)
8	100	15	8	3	—	w	170 (w), 153 (2)
9	100	10	80	w	w	5	285 (8)

b) Phosphorothiolates and Phosphorodithioates

Compound	$(M)^{+\cdot}$	$(M+1)^+$	$(M+2)^+$	$(Z)^+$	$(M-Z)^+$	$(M-SZ)^+$	Other m/z (%)
10	100	13	10	—	—		
11	90	18	26	100	31	90	155 (65), 185 (33)
12	100	14	20	2	4	3	186 (15)
13	100	5	6	w	vw	vw	
14	100	15	9	78	24	18	189 (5)
15	100	44	34	95	35	5	
16	100	60	14	—	vw	3	149 (17)
17	100	20	52	7	3	4	
18	100	14	19	7	w	2	368 (2)
19	8	100	20	18	4	3	143 (57)

c) Other Organophosphorus Pesticides

Compound	$(M)^{+\cdot}$	$(M+1)^+$	$(M+2)^+$	$(Z)^+$	$(M-Z)^+$	$(M-SZ)^+$	Other m/z (%)
20	14	100	48	—	8	31	112 (18)
21	—	80	—	—	100		259 (48), 261 (13)

β-cleavage to form the ion $(Z)^+$. In addition, most of the substances exhibited the fragments $(M - X_1Z)^+$ by the α-cleavage. Furthermore, for those compounds in which the Z moiety is aliphatic, the fragmentation is more pronounced than for those with an aromatic moiety, for example, in the cases of 1, 10 and 11. The direct α- and β-cleavages forming the complementary fragments, almost without exception, were observed in the FD spectra, so that interpretation is easy. In the mass spectra of several of compounds such as 10 and 21, the dimeric ion $(2M)^{+\cdot}$ and protonated dimer $(2M + H)^+$ were recorded. The occurence of these ions can be helpful in confirming the identification of unknown compounds.

The FD spectrum of **9** (Figure 1a), obtained in the temperature range close to the BAT, demonstrates the characteristic behaviour of organophosphorus pesticides. Compared with its EI mass spectrum, where the molecular ion was not observed[26] an intense molecular ion group was recorded. The $(M+2)^+$ ion corresponded to the base peak. The $(M)^{+\cdot}$ and $(M+4)^+$ ions have the abundances of 80% and 30% respectively. It should be noted that the isotope distribution in this group of peaks was changed because of proton-transfer reactions which take place during desorption. In addition, as shown in Figure 1a, a negligible peak at m/z 285 for the ion $(M-Cl)^+$ was also observed.

The pattern in the FD mass spectra is highly dependent on the experimental conditions, especially on the emitter temperature. Heating of the emitter above the BAT will result in thermal-induced fragmentation which makes the spectrum more complicated. Figure 1b shows the averaged (8 scans) FD spectrum of **9** obtained at an emitter heating current between 0 and 10 mA. The $(HOZ)^+$ fragment at m/z 196 whose relative abundance is 1% was produced by the typical α-cleavage concomitant with proton transfer. These characteristic fragments are also observed in the FD spectra of the **1–8**. In addition, the fragment $(OZ-Cl)^+$ of **9** at m/z 160 is produced by the α-cleavage accompanied by loss of a chlorine atom. The molecular ion at m/z 320 was recorded as base
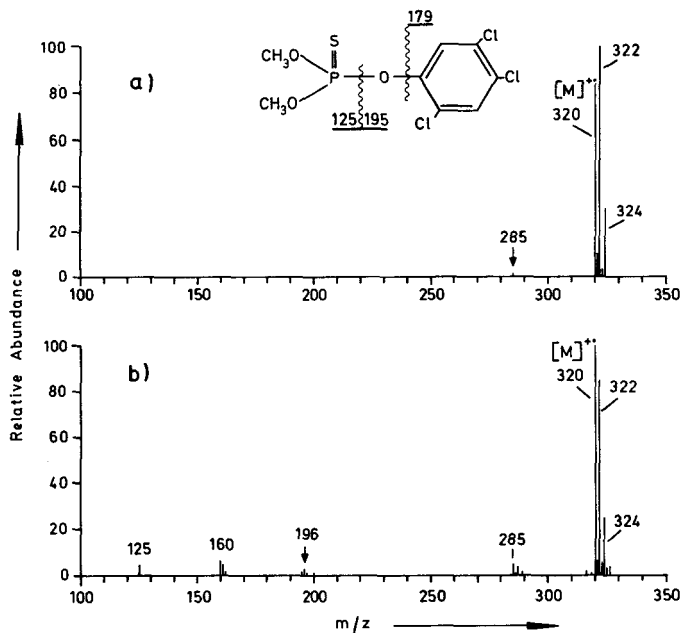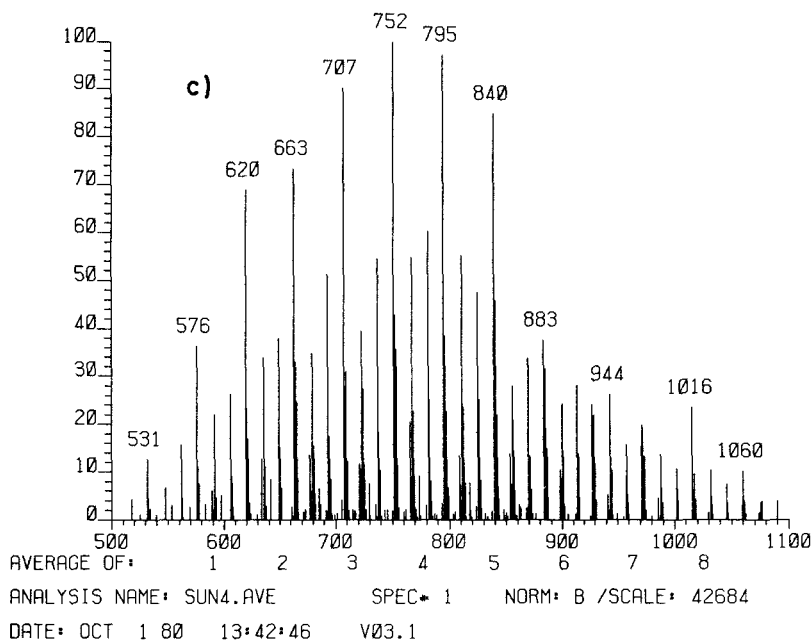
FIGURE 1   Field desorption mass spectra of ronnel obtained at an emitter heating current:
(a) 0 mA; (b) 0–10 mA and (c) 30–50 mA. The spectra were obtained from a STATOS 33
printer/plotter using the Varian MAT SS 200 data system for storing and processing of the
electrical recorded FD ions.

peak. Figure 1c shows the averaged FD spectra of the ronnel standard
(98 %) obtained at an emitter heating current from 30 to 50 mA. The
clusters of peaks in the upper mass range at m/z 520–1094 are
characteristic for the mass spectral pattern of a mixture of $C_{37}-C_{78}$
aliphatic hydrocarbons, and are explained by the presence of lipid
impurities in the standard sample of ronnel.

The FD mass spectrum of **14** obtained at an emitter heating current
from 0 to 10 mA is shown in Figure 2. As compared with its EI mass
spectrum,[27] where the molecular ion was not observed, the molecular ion
at m/z 317 is recorded as the base peak. The $(Z)^+$ fragment at m/z 160 is
due to the β-cleavage of the X_1-Z bond and charge localization at the Z
moiety. Its elemental composition corresponds to $(C_8H_6N_3O)$ (theor.
160.0511; exp. 160.0496). The complementary ion at m/z 157 is displayed
with a relative abundance of about 30%. Its elemental composition is
$C_2H_6O_2PS_2$ (theor. 156.9547; exp. 156.9563). Moreover, the ion at m/z 125
formed by α-cleavage is also found and its elemental composition is
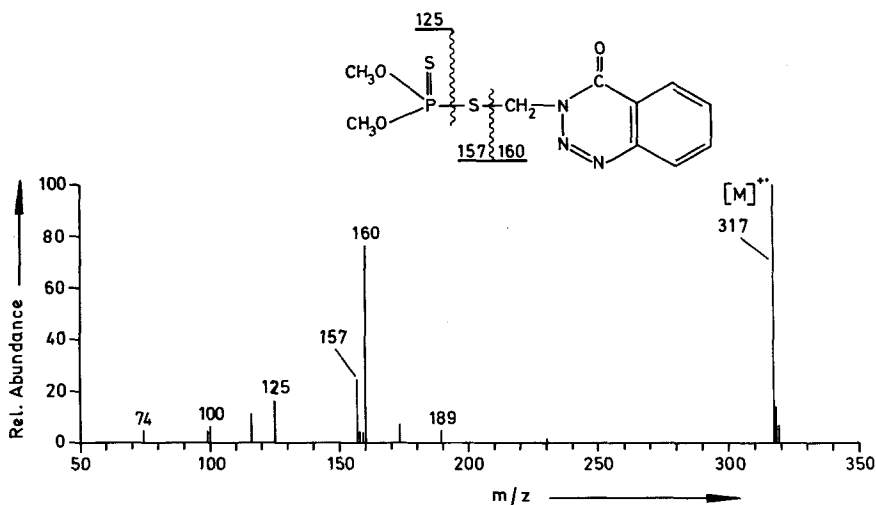$C_2H_6O_2PS$ (theor. 124.9826; exp. 124.9881). The fragmentation of

FIGURE 2   Field desorption mass spectrum of guthion recorded at an emitter heating current from 0 to 10 mA.

substances **10–13** and **15, 17–19** shows similar characteristics in their FD mass spectra.

The FD spectrum of **16** obtained at an emitter heating current from 0 to 40 mA showed no fragments resulting from the characteristic β-cleavage forming the ion at m/z 173 but a relatively weak peak at m/z 125 produced by α-cleavage can be observed. The major fragment ion in the spectrum was the ion at m/z 149. This finding was also recorded in the FI mass spectrum by Damico et al.[8]

The structures of **20** and **21** are different from those of the organophosphorus esters reported above. For the **21**, the moiety Z is directly associated with the P atom. In the FD spectrum of **21** the ion at m/z 109 was recorded for the base peak. It resulted from the P–C bond cleavage with charge retention on the phosphorus moiety. The elemental composition is $C_2H_6O_3P$ (theor. 109.0055; exp. 109.0013). A cluster of peaks at m/z 257, 259 and 261 with relative intensities 80%, 60% and 20% respectively could be identified with the $(M+1)^+$, $(M+3)^+$ and $(M+5)^+$ ions. Further, a fragment at m/z 117 due to the CCl_3 group was also observed in the spectrum. This terminal cleavage appears to be a general feature of compounds containing the CCl_3 group.[28]

It should be noted that the abundance of the molecular ion of **1** obtained at 0mA emitter heating current ($\sim 50°C$) was 10% only. Under these conditions an ion at m/z 279 was recorded as base peak. Two facts,

however, indicate that this signal resulted from an impurity. No cluster ions are observed which could be associated with the presence of chlorine atoms. Moreover, the ion at m/z 279 is observed frequently at low emitter heating currents and has been identified to be due to a phthalate plasticizer from plastic sample containers.[29, 30]

Limit of detection

The limit of detection of FD-MS, in general, is dependent on both the registration method and the property of the substances to be analysed. As reported previously,[16,17] for the FD analysis of organic nitrogen-containing pesticides, an amount of substance in the μg range is required to generate sufficiently intense ion currents of molecular and fragment ions for photographic detection at a resolution of 20 000. Electrical detection is more sensitive in a limited mass range and at low resolution. A further reason for this is that the desorption temperature which produces the most intense ion current of the molecular ion group can be selected on-line with the FD results. Therefore, ng or even pg samples are sufficient for detection. However, some of the organophosphorus pesticides as pure standards have a relatively high volatility and desorb from the emitter at ion source temperature (0mA, ~50°C) and before optimal adjustments for recording are set. In these cases the amount of the sample analyzed may be larger than that required for the detection of the other pesticides of low volatility. With respect to latter, Figure 3 shows, for instance, the FD spectrum of 5 ng of guthion obtained by repeating the magnetic scan and accumulating the ion signals on a multichannel analyzer. The signal to noise ratio obtained is about 100:1.

The measurement of the isotopic ratios for the peaks at m/z 317, 318 and 319 is given in Figure 3. These experimental data for the ions m/z 319 and m/z 320 are consistent with the theoretical calculation. An exception is the ion at m/z 318 which differs about 2.8 % from the theoretical value. This results most probably from proton-transfer reactions occurring during field desorption.

Determination of the isotopic ratios of the molecular ion group by FD-MS can provide important supplementary information for identification,[31] particularly, when no other analytical method is employed.[32] However, attention must also be paid to the fact that ion-molecule reactions on the emitter may change the isotope ratios.[33]

Analyses of mixtures

In contrast to organochlorine pesticides, the organophosphorus pesticides are easily degraded in the environment to form a number of nonmetabolic and metabolic substances. The characteristically high relative abundances

of molecular or quasimolecular ions and the minimal fragmentation of organophosphorus pesticides in FD-MS provide conditions for direct analyses of these compounds in mixtures without preliminary separation. In order to evaluate the potential of the method, a synthetic mixture of three standards: guthion, ronnel and trichlorphon was prepared and investigated. The averaged FD spectrum obtained at an emitter heating
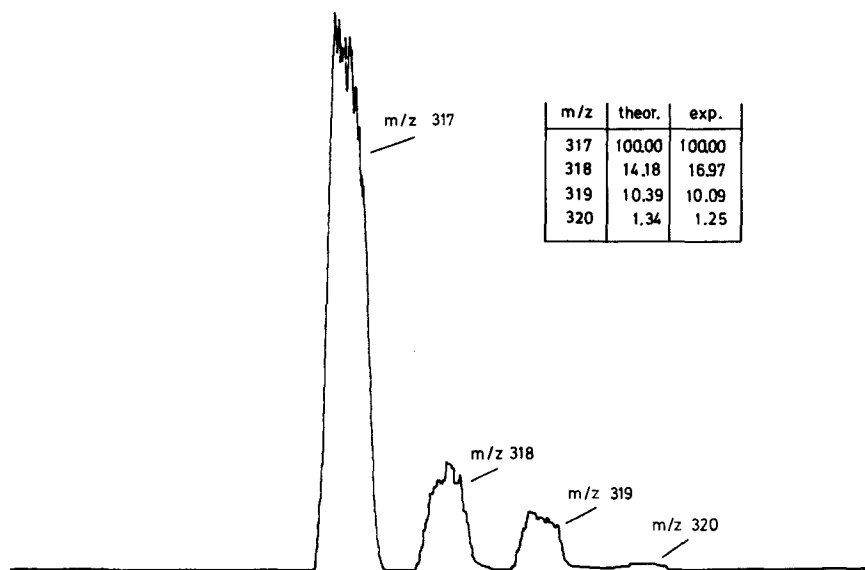
m/z	theor.	exp.
317	100.00	100.00
318	14.18	16.97
319	10.39	10.09
320	1.34	1.25

FIGURE 3   Intergrated registration of FD ion signals of guthion with electrical detection and accumulation over 22 scans on a Tracor Northern NS–570A multichannel analyzer (16K). The output of the digital signal was displayed with a Hewlett Packard 7004B X-Y recorder. The mass range was from m/z 310 to m/z 325. The emitter heating current was from 0 to 30 mA. Five ng guthion was applied to the emitter. The theoretical and experimental values of the direct isotope determination are given in Figure 3.

current up to 10 mA is shown in Figure 4. The mixture exhibited the same ions as the sum of the spectra of the individual compounds, although it is possible that interaction between compounds of the mixture take place in absorbed surface layer. However, no peaks detected indicate these chemical interaction. The peaks at m/z 320, 317 and 257 correspond to the molecular and quasimolecular ions of ronnel, guthion and trichlorphon, respectively. The relatively abundant ions at m/z 160, 125 and 109 are their characteristic fragments as described above.
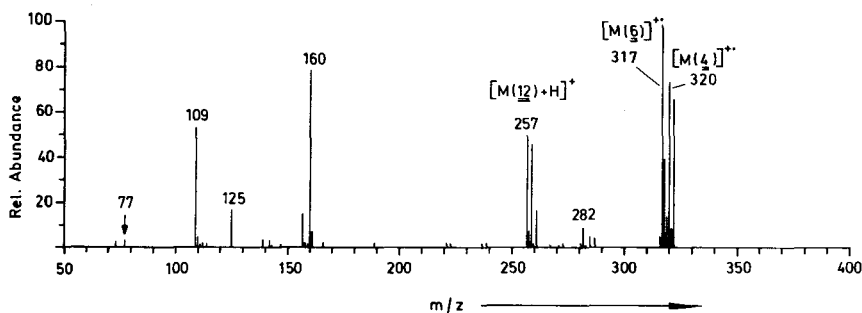
FIGURE 4 Field desorption mass spectrum of a mixture of ronnel, guthion and trichlorphon. Desorption program as described for Figure 1.

Identification of organophosphorus pesticides from water extracts

Organophosphorus pesticides such as dimethoate, trichlorphon as well as dichlorvos are widely used in China for the protection of agricultural products. In mass spectrometric investigations of environmental samples, particular attention is paid to the molecular ions produced by these substances. Figure 5 shows the electrically registered FD mass spectra of an extract of a sample of river water. These spectra were recorded and averaged at an emitter heating current between 0 and 20 mA. The FD spectrum from mass 50 to mass 500 exhibits the molecular ion of dimethoate at m/z 229 with high relative abundance.

In order to confirm the molecular ion of **10** in waste water at m/z 229 corresponding to the elemental composition $C_5H_{12}O_3NPS_2$ by *direct isotope determination*, repeated magnetic scanning in this mass range m/z 220–235 was done and the FD spectra were accumulated by the multichannel analyzer. The results are shown in Figure 6a and compared with that of standard dimethoate obtained at similar experimental conditions (Fig. 6b).

The theoretical values (in %) for the isotope ratios of the peaks of dimethoate (**10** $C_5H_{12}O_3NPS_2$) at mass 229, 230 and 231 are 100, 7.85 and 9.76 respectively. The experimental values in the FD mass spectrum for the standard of **10** (Figure 6b) are m/z 229 (100%), m/z 230 (7.77%) and m/z 231 (9.15%). For the FD signals of **10** identified in the water extract (Figure 6a) the found isotopic distribution was: m/z 229 (100%), m/z 230 (20.26%) and m/z 231 (9.48%). The data for the peak at m/z 231 obtained from the water extract are consistent with that from the standard and are within the experimental error of a few tenths of a percent in agreement with the theoretical values. However, the peak at m/z 230 is more than two times higher as could be expected from its theoretical
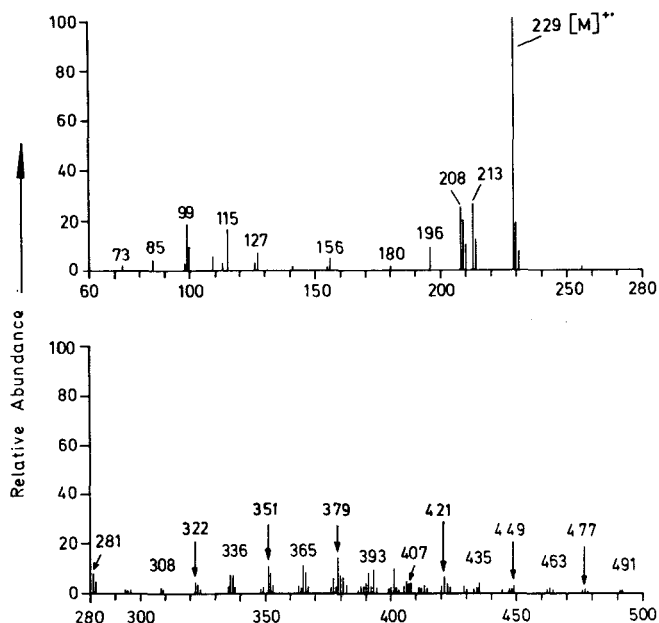
FIGURE 5   Field desorption mass spectrum of an extract of waste water (23 July 1980, Liang Shui river, Peking). The emitter heating current was regulated from 0 to 20 mA. The other experimental conditions were as described for Figure 1. Note that the doubly charged ion at m/z 98.5 has been shifted to the next nominal mass m/z 99 due to the operating mode of the Varian SS200 data system.

value. Since both spectra in Figure 6b (standard) and Figure 6a (water sample) have been obtained under the same experimental conditions (0–15 mA emitter heating current), the enhancement of this peak results most probably from proton-transfer reactions with acidic impurities present in the water extract. It is noteworthy that the isotope ratios of m/z 231 are correctly found in both cases which excludes the superposition of an FD signal of a major ($\pm 0.3\%$) impurity on m/z 230.

Further identification is based on accurate mass measurements using the peak matching technique. High resolution data for the peak at m/z 229 gave a found mass 228.9960 (theor. 228.9995). In addition, the spectra of standard dimethoate obtained previously using both electrical and photographic detection at the emitter heating current from 0 to 30 mA showed several abundant fragments: the ion at m/z 196.0197 $(M-H_2S+H)^+$, the doubly charged ion at m/z 98.4999 $(M-S)^{++}$, the ion at m/z 125.9940 $(M-SZ+H)^+$ and the ion at m/z 73.0527 $(Z+H)^+$. These ions were also observed in the FD spectrum of the waste water sample
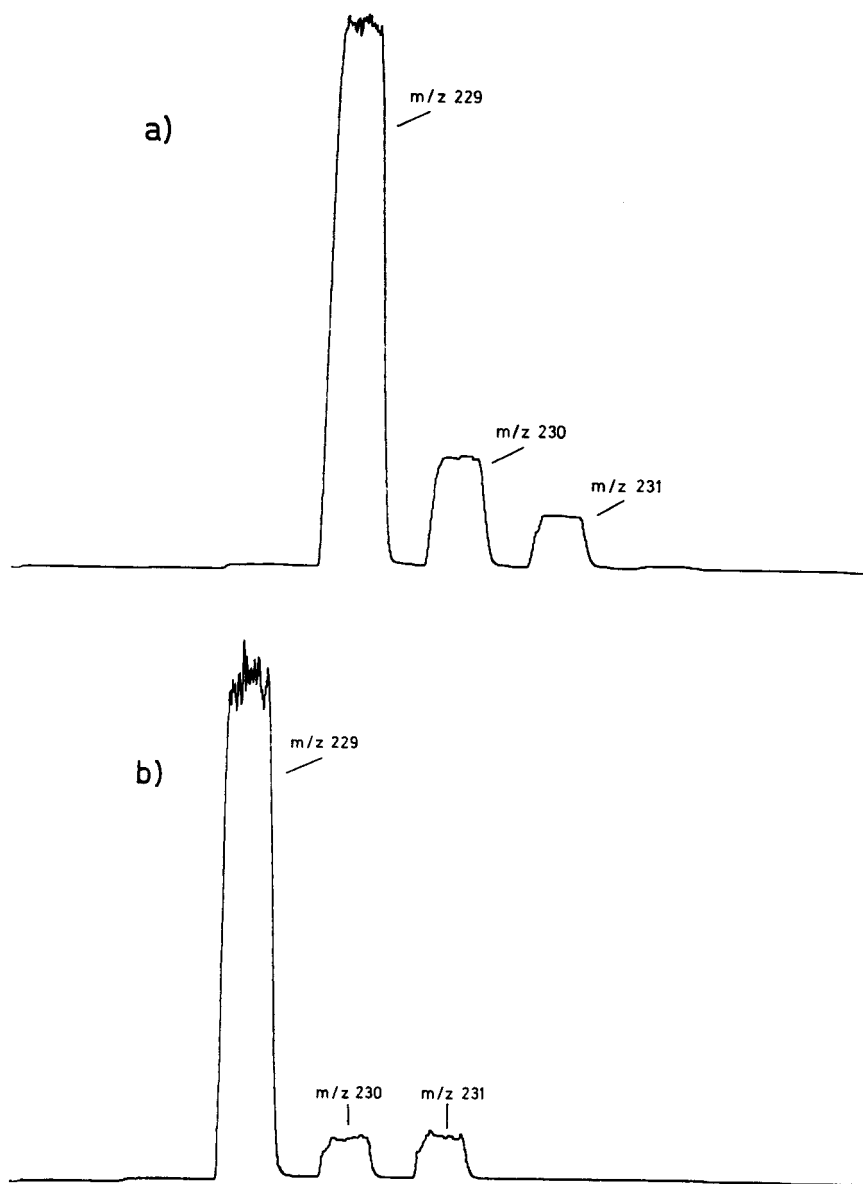
FIGURE 6 Comparison of the pattern of the molecular ion group of the dimethoate: (b) standard and (a) identified dimethoate in waste water. The experimental conditions were as described for Figure 3 except the emitter heating current which was 0–15 mA in this experiment.

displayed in Figure 5. Therefore, the compound found in waste water unambiguously is identified as dimethoate.

It should be noted that a peak at m/z 213 (30%) was observed which was not found in the spectrum of standard dimethoate. It is assumed that this ion is due to dimethoxon, an oxygen analog of dimethoate ($C_5H_{12}O_4NPS$, theor. 213.0224; exp. 213.0210). The peak at m/z 180 (2%) appears to be a fragment from dimethoxon $(213 - H_2S + H)^+$.

As shown in the spectrum, there is a cluster of signals in the mass range from m/z 282 to m/z 492. The difference between neighbouring peaks is 14 mass units. This is a characteristic feature of a FD mass spectrum of a mixture of C_{20}–C_{35} alkanes. Therefore, it is reasonable to assume the sample contained mineral oil as an impurity. Other organophosphorus pesticides than dimethoate were not found in this extract of waste water. Although the water extract was not cleaned up and was a very complex mixture, the investigated pesticides have been correctly selected under field desorption conditions and these contaminants will not interfere with the reliable identification of the biocides.

CONCLUSION

This investigation is a first report on the application of FD-MS in China. Since now combined EI/FD instruments are becoming available, both, the methodological and analytical aspects of the technique, could serve as a guideline for further work.

The characteristic features of FD spectra obtained from twenty-one commonly used organophosphorus pesticides are described and as expected, most of the substances examined showed high molecular ion abundances and characteristic fragments resulting from direct bond cleavages. Thus, the main advantage in the analysis of waste water is that mixtures containing traces of biocides, in particular of low volatility, can be analysed directly without preliminary separation and chemical derivatization. The results obtained in this study indicate that FD-MS is a useful technique for screening the parent biocides and their metabolites and degradation products in surface water.

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