

Degradation of Chlorpyrifos-Ethyle by Gamma Radiation

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ABSTRACT/RESUME

Abstract: Chlorpyrifos-ethyle is an organophosphorus pesticide causing problems in the central and peripheral nervous system, respiratory system, and the digestive tract of human beings and animals. This study concerns the degradation of chlorpyrifos-ethyle dissolved in acetonitrile by exposition to ionizing radiation. The solution was irradiated to absorbed doses varying from 1 to 50kGy, using a ⁶⁰Co gamma source. The variation of chlorpyrifos-ethyle concentration as a function of absorbed dose was followed by HPLC analyses. The results showed that the chlorpyrifos-ethyle was completely degraded at the dose of 50kGy. The identification of by-products formed during radiation degradation process of chlorpyrifos-ethyle was made using gas chromatography associated to mass spectrometry (GC-MS). Consequently, three by-products were identified namely: 2-hydroxy-3,5,6,- trichloropyridine (TCP), phosphoric acid, diethyl 3,5,6-trichloro-2-pyridinyl ester, and 2-furancarboxaldehyde, 5-(hydroxymethyl).

I. Introduction

Chlorpyrifos-ethyle (CPF-E) which is commonly used in Mediterranean countries often ends up in aquatic environment carried by wind and agricultural runoff [1]. Its residues may be detected in the environment from months to years [2]. The CPF-E affects many organs of the body [3]. A large volume of literature has been published in the last 15 years on the degradation of pesticides pollutants. Various research groups in the world have developed some physical-chemical techniques to remove or degrade pesticides. Among them, one can cite X-ray irradiation [4], photocatalytic oxidation [5,6], electron beam radiation [7]. In addition to these techniques, gamma irradiation has been successfully used to degrade pesticides [2,7,10]; in most cases, the products of radiolysis have been identified, but mechanistic studies leading to their formation are relatively few. In this work, we have focused on the degradation kinetics of CPF-E in acetonitrile by gamma radiation. The analyses have been carried out by HPLC. Thus the

major concern of this study is the determination of the main by-products formed using GC-MS technique.

II. Experimental procedure

II.1. Chemicals

The CPF-E (0,0-diethyl-3, 5,6- trichloro-2-pyridyl phosphorothioate), 99.8% purity purchased from CHEMINOVA was used without any further purification. The HPLC-grade acetonitrile was supplied by MERCK, Darmstadt, Germany. The glacial acetic acid was supplied by SIGMA. Stock solution of CPF-E was diluted in acetonitrile and protected from light and stored at 4°C.

II.2. Irradiation procedure

The samples in glass vials containing 10 ml of CPF-E stock solution (C₀-0.5g/l) were irradiated with C₀-60 gamma rays at the doses of 1, 5, 10, 20 30 40 and 50 kGy. The irradiation was carried out at room temperature at a dose rate of 38.42Gy /min. The Fricke dosimeter system was used to determine

the dose rate.

II.3. Analysis of the irradiated solutions by HPLC

The HPLC analyses were carried on chromatograph Waters 501 equipped with Waters 484 Tunable Absorbance Detector and a C18 column (3.9mm x 150mm). Chromatographic conditions were as follow: the mobile phase consisting of a mixture of acetonitrile, water and glacial acetic acid in volume proportions of 82:17.5:0.5 was pumped at 1ml/min flow rate. The detection was realized at the UV wavelength of 300nm. The injection volume was 20 μ l. The degradation rate DR (%) of the CPF-E was calculated using the following formulae:

$$DR = 100 - \frac{h_D}{h_0} \cdot 100 \quad (1)$$

Where: h_0 is the height of the control sample peak and h_D is the height of the irradiate solution peak.

II.4. Analysis of by-products by GC-MS

The identification of by-products was carried out on the solution of CPF-E ($C_0=0.5\text{g/l}$), which was irradiated at 50kGy. GC-MS analyses were performed on Agilent Technologies HP 6890N Network GC and Agilent Technologies HP 5973Network Mass selective Detector, equipped with an HP5MS column of 30cm length and 0.25mm i.d; 0.25 μ m film thickness. The separation of by-products was conducted under the following chromatographic conditions: injector temperature 250 $^{\circ}$ C, oven temperature program from 120 $^{\circ}$ C - 270 $^{\circ}$ C at the rate of 6 $^{\circ}$ C/min and isotherm at 270 $^{\circ}$ C during 5min. Helium was used as carrier gas at a flow rate of 1ml/min and the volume injected was 5 μ l. The temperature of the ion source and the interface were set at 230 $^{\circ}$ C and 280 $^{\circ}$ C respectively. The MS operated in electron impact ionization mode with a potential of 70eV and the spectra were obtained at a scan range from m/z 18-550.

III. Results and discussion

III.1. Variation of CPF-E concentration as a function of irradiation dose

The HPLC chromatogram revealed the CPF-E peak at the retention time of 2.2min. The height of the CPF-E peak decreased progressively with the increase of the absorbed dose and disappeared completely at 50kGy. New peaks observed at different retention times were attributed to the degradation products.

Using the calibration curve ($R^2=0.9961$), the peak heights were converted into concentrations. The variation of the CPF-E concentration as a function of absorbed irradiation dose is represented on figure1.

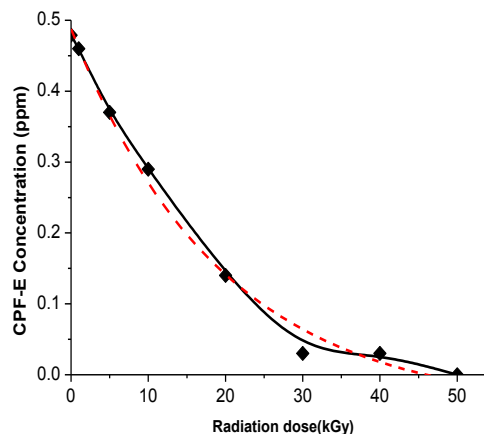


Figure1. Irradiation effect on the concentration of CPF-E.

The CPF-E concentration in the solution decreases exponentially with the absorbed dose. The fit from the experimental data gave the following exponential function:

$$C = C_0 e^{-D/D_t} \quad (2)$$

With a correlation coefficient of: $R^2 = 0.99331$

Where: C : Concentration of CPF-E after irradiation; C_0 : initial concentration of stock solution; D : irradiation dose; D_t : dose constant (or the characteristic dose).

This drastic decrease of CPF-E concentration with the increase of radiation dose denotes that gamma radiation is efficient in degrading the CPF-E. The results obtained for the irradiation effect on the concentration of CPF-E, are comparable to those reported by [4].

The degradation rate was followed using HPLC analyses. The HPLC histograms on Figure 2 show the progressive degradation of CPF-E according to the absorbed doses.

One hundred percent of CPF-E was detected at 0kGy irradiation (control). Thus, the histogram shows that only 3% degradation of the pesticide was observed starting from 1kGy, and continues to increase to 21% at 5kGy and reaches 90% at 30kGy. The CPF-E was completely degraded at 50kGy as shown on Figure 2. It has been reported [2] that a complete degradation of the same pesticide in acetonitrile was obtained at 10kGy for a concentration of 13.7 μ mol/l.

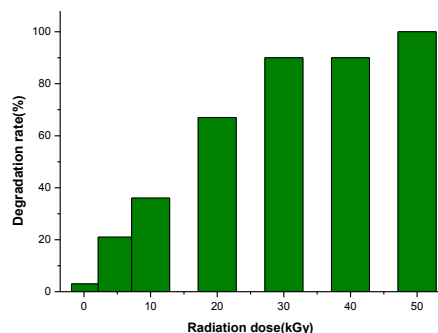


Figure 2. Degradation rate of CPF-E vs irradiation dose.

III.2. GC-MS analysis of CFP-E solution irradiated at 50kGy

III.2.1. GC-MS analysis of the CPF-E control solution

Figure 3 shows the GC-MS chromatogram of unirradiated CPF-E solution. The CPF-E peak appeared at the retention time of 17.33 minutes.

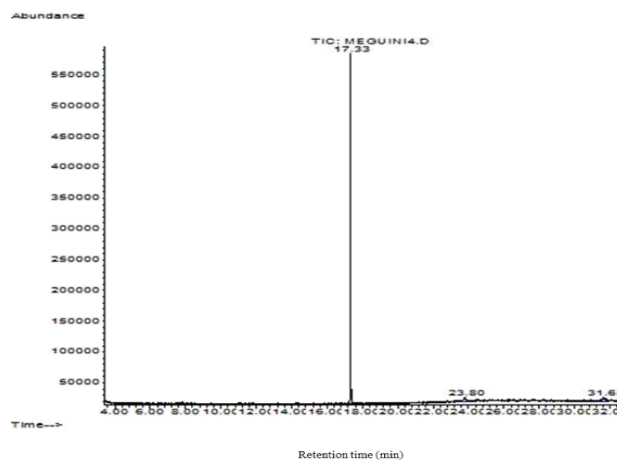


Figure 3. GC-MS chromatogram of unirradiated CPF-E solution

III.2.2. GC-MS analysis of the irradiated solution

Figure 4 shows the appearance of three peaks corresponding to the retention times of 4.37, 8.49 and 17.17 minutes which are attributed to the metabolites resulting from the degradation of the CPF-E. The identification program of NIST library has identified the by-products formed with a fit value higher than 70% in all cases. The mass spectra of these compounds are listed in table 1. The identified by-products of CPF-E are summarized in Table 1 along with their retention

times and the characteristic ions of the mass spectra using the identification program of NIST library.

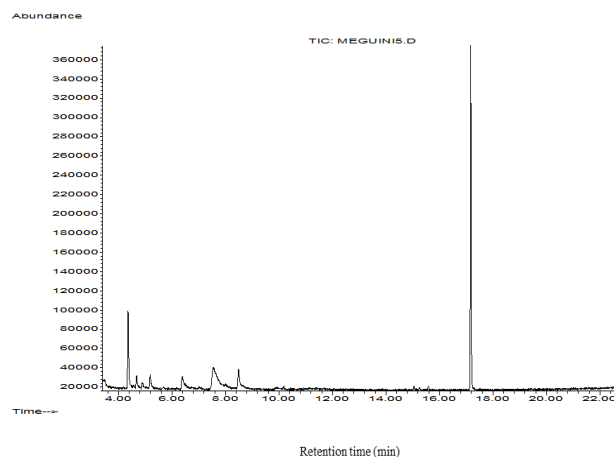


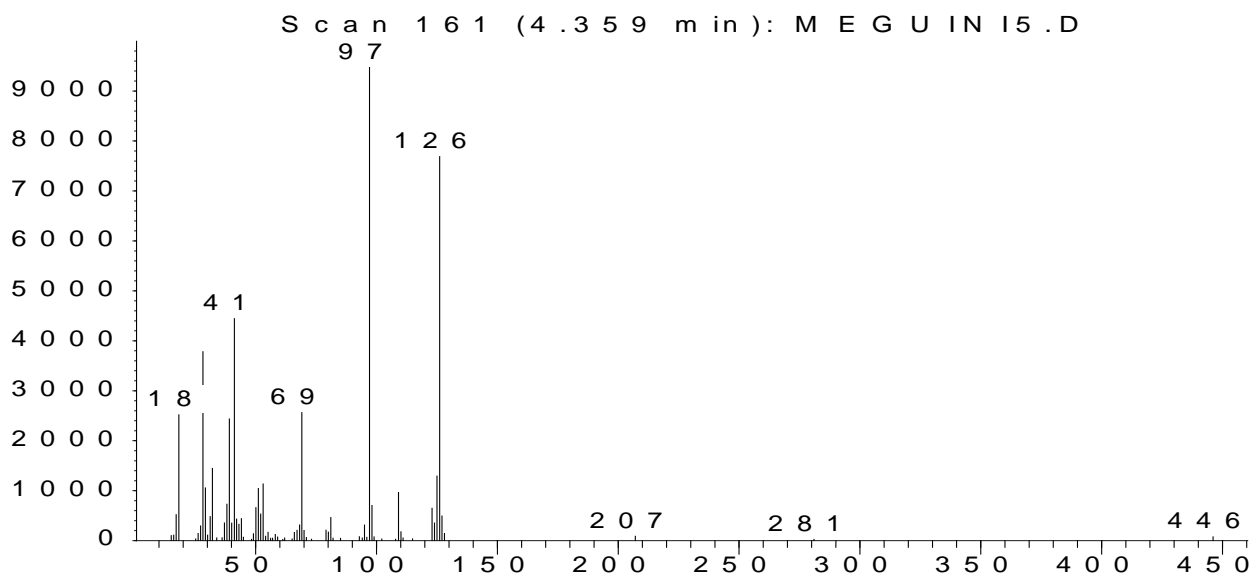
Figure 4. GC-MS chromatogram of CPF-E solution irradiated at 50kGy

Indeed, the product which completely disappeared is transformed into degradation products such as 2-furancarboxaldehyde,5-(hydroxymethyl) ; 2-hydroxy-3,5,6-trichloropyridine (TCP) and phosphoric acid, diethyl 3,5,6-trichloro-2-pyridinylester (Chlorpyrifos- oxon). Figure 5 shows the mass spectra of CPF-E and that of the compounds C1, C2 and C3 resulting from the degradation of the pesticide during the radiation process. These compounds were identified as C1: 2-furancarboxaldehyde,5-(hydroxymethyl) ; C2: 2, hydroxy-3, 5,6-trichloropyridine (TCP) and C3: phosphoric acid, diethyl 3,5,6-trichloro-2-pyridinylester (chlorpyrifos-oxon) with a good matching using NIST library. The formation of C2 and C3 compounds has been reported in the literature as a hydrolysis and desulfuration products, respectively [2, 7]. Under gamma irradiation the desulfuration which leads to the formation of chlorpyrifos-oxon may be attributed to the oxidation process. The mechanism could be that of the action of ozone on the double bound P=S before the breakdown of the molecule as reported [11]. Indeed, when irradiation is performed in the presence of air, ozone is formed as a result of the transformation of oxygen by gamma rays. It has been reported [12], that the third compound (chlorpyrifos-oxon) is degraded to TCP by hydrolysis process. This means that the TCP is the main transformation product of CPF-E. In addition to the two well identified metabolites C2 and C3, our GC-MS analyses revealed the presence of another by-product C1. This by-product which was identified as 2-furancarboxaldehyde,5-(hydroxymethyl) with more than 70% matching to NIST library, has not been reported.

Table 1 . GC-MS retention time (R_t) and spectral characteristics of CPF-E by-products identified

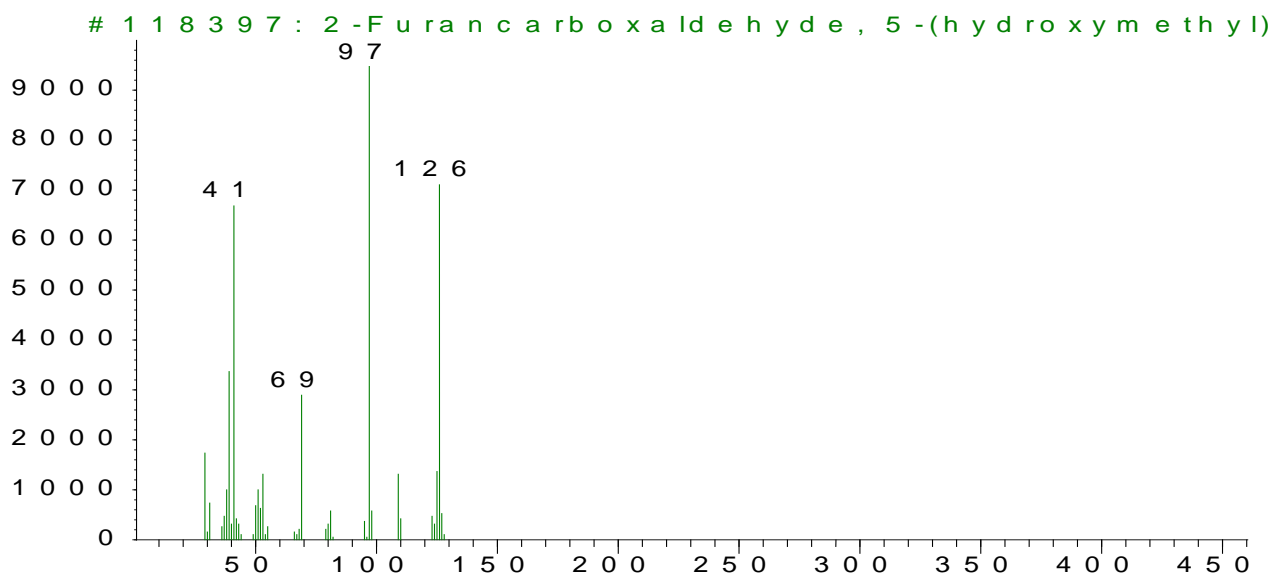
Compounds (C)	R_t (min)	Characteristics ions (m/z)
1. 2-furancarboxaldehyde,5-(hydroxymethyl)	4.359	126,97,69,41.
2. 2-hydroxy-3,5,6-trichloropyridine (TCP)	8.494	197,169,134 ,107,72,32.
3. Chlorpyrifos-oxon	17.17	335, 298, 270, 260, 197, 180, 169,133.
Chlorpyrifos-ethyle	17.33	314,286, 258, 213,197, 169, 144,125.

Abundance



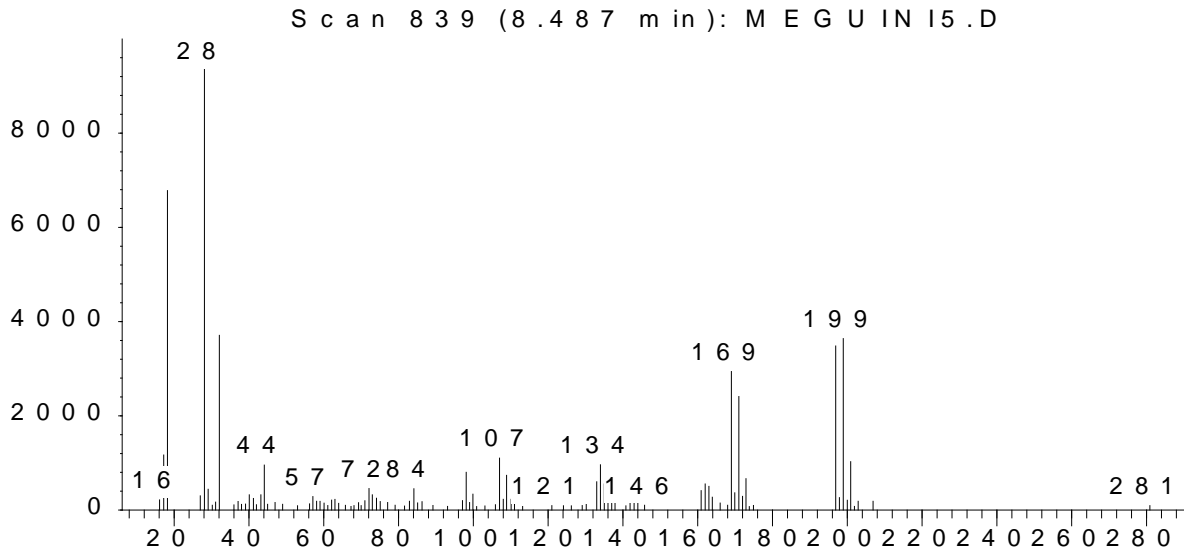
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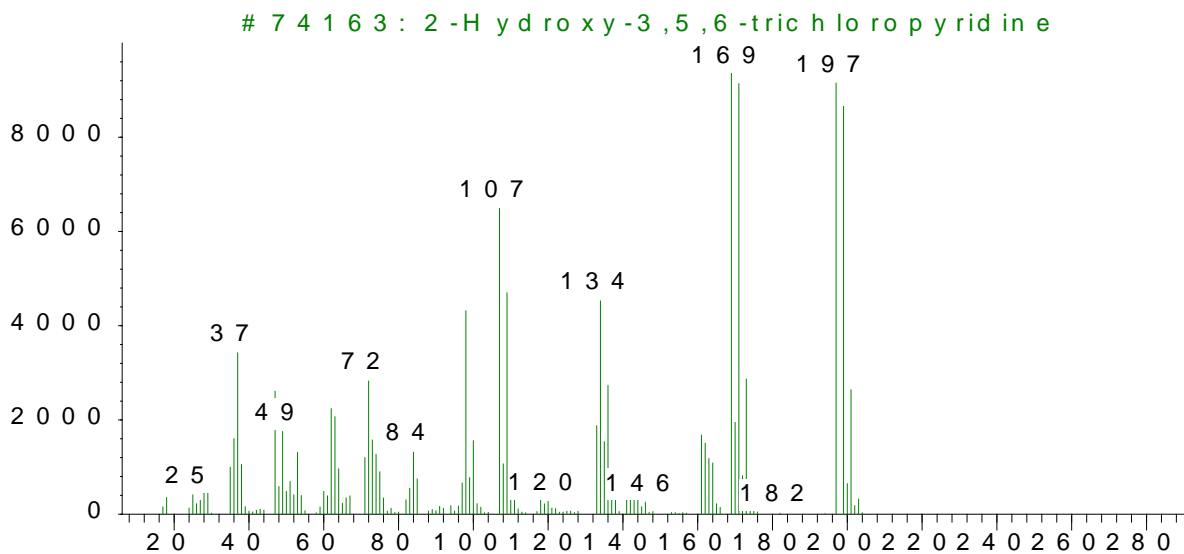
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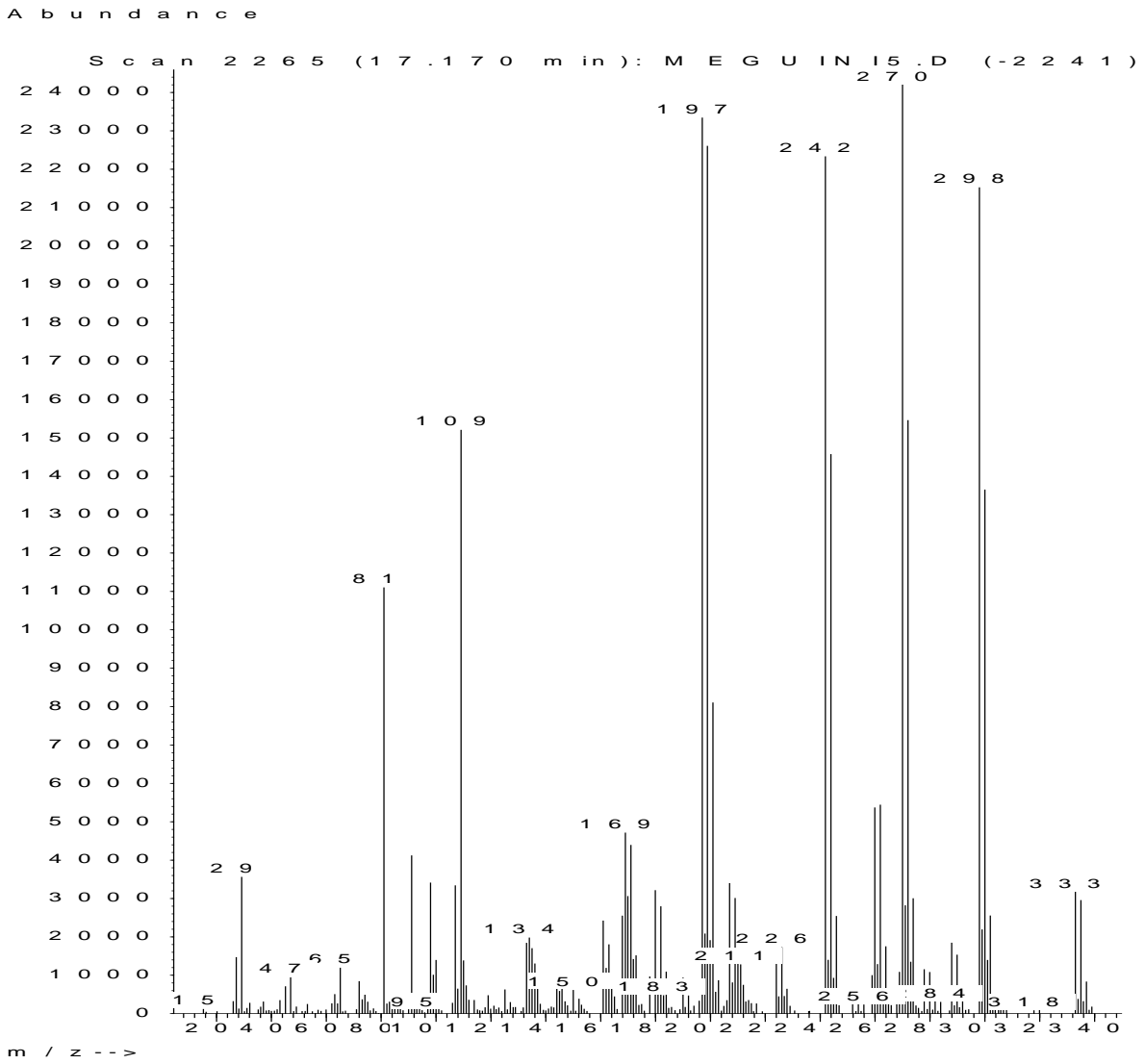


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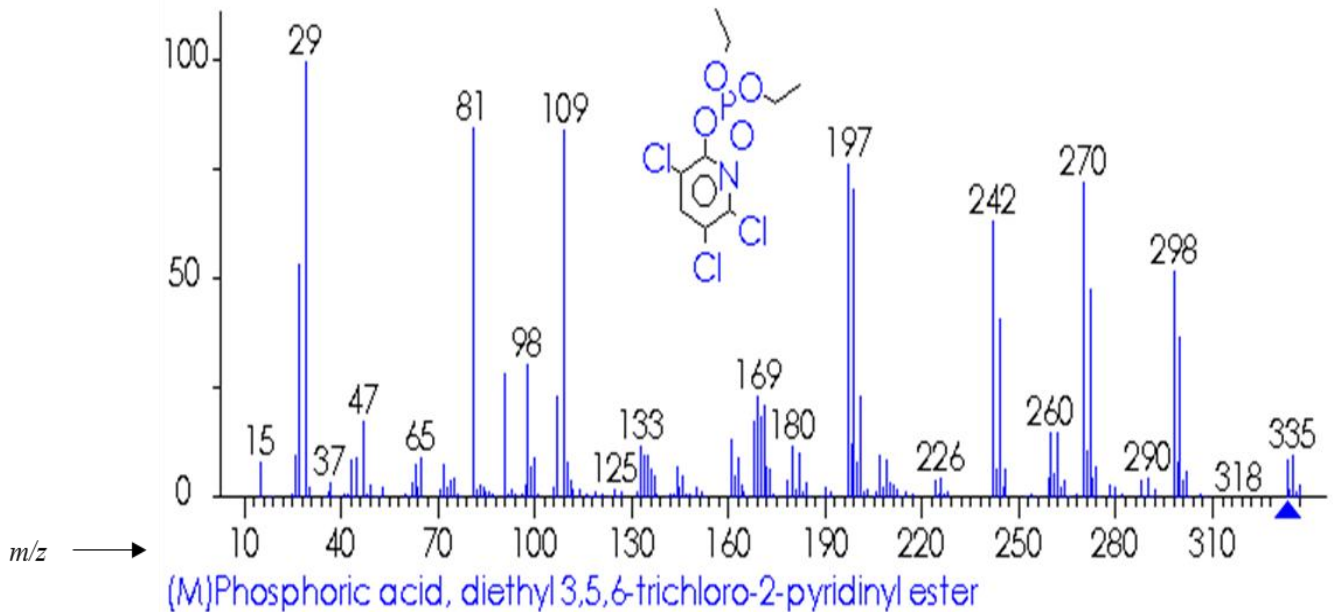
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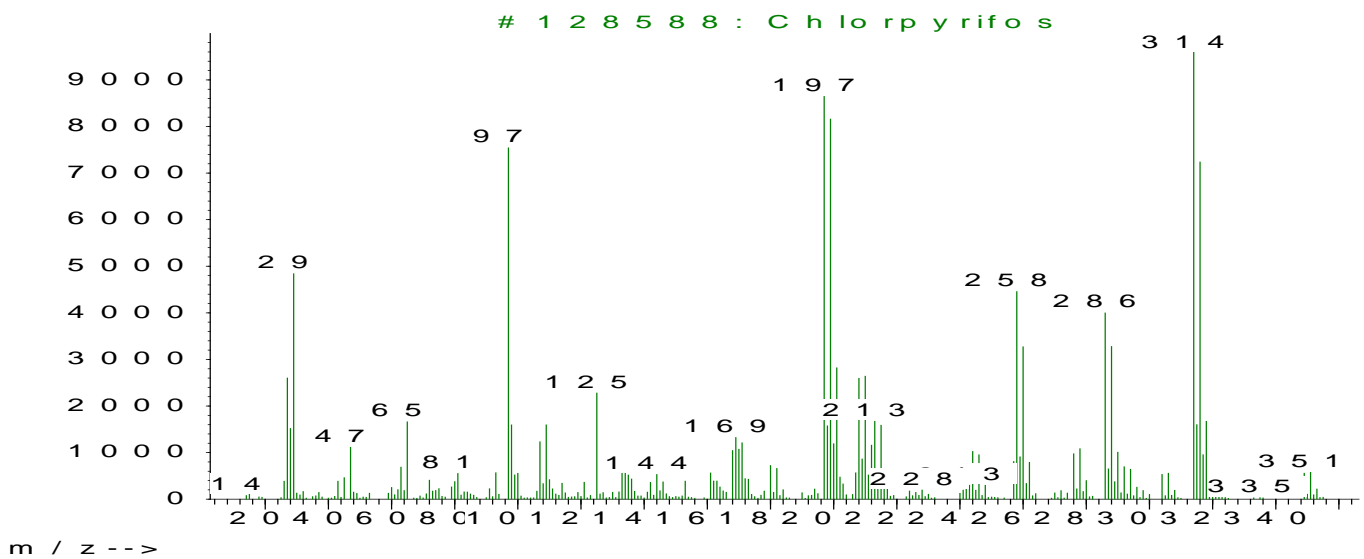
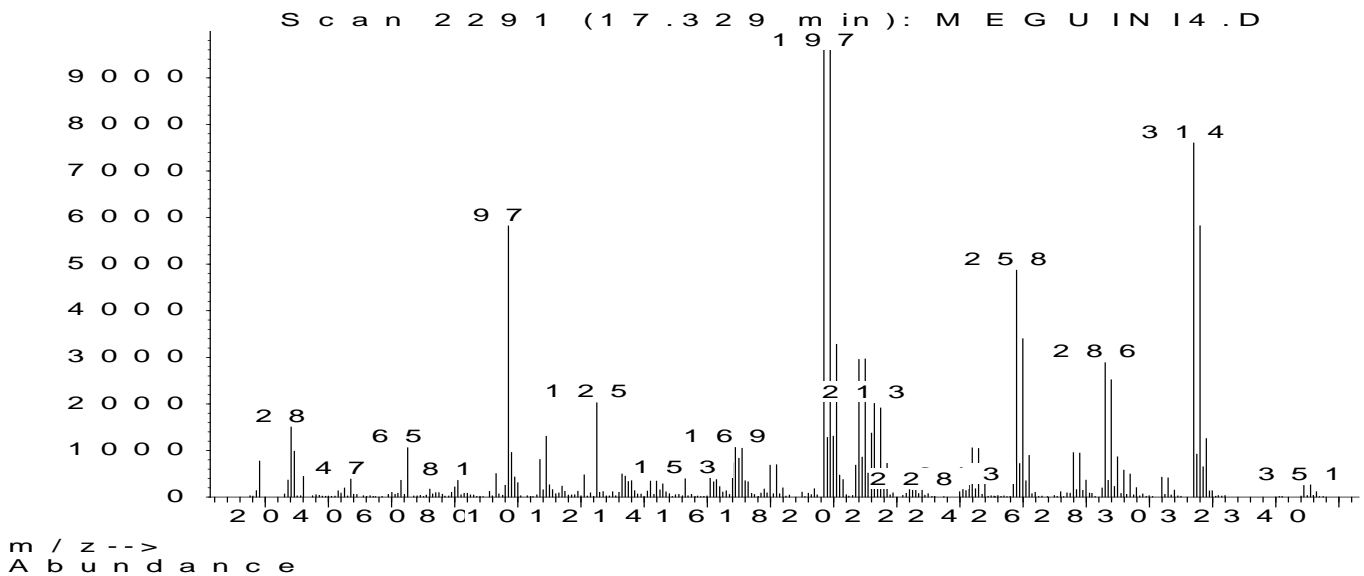


Figure5. Mass spectra of CPF-E and its degradation products (C1, C2 and C3) formed during gamma radiation (50kGy).

IV. Conclusion

In this study, a solution of chlorpyrifos-ethyle in acetonitrile at a concentration of 0.5g/l was exposed to a large dose range of gamma irradiation. The pesticide was efficiently degraded by gamma radiation at the absorbed dose of 50kGy. The HPLC analysis showed the presence of three major degradation products formed during the radiation process of CPF-E. GC-MS analysis allowed the identification of the desulphuration product and the hydrolysis product, which are

respectively, the phosphoric acid, diethyl 3,5,6-trichloro-2-pyridinyl ester (chlorpyrifos oxon) and the 2-hydroxy-3,5,6-trichloropyridine (TCP).

In addition, the GC-MS analysis showed the presence of the 2-furancarboxaldehyde, 5-(hydroxymethyl), which seems to be a by-product resulting from the radiolysis of chlorpyrifos-ethyle, but not reported anywhere on the literature.

Gamma irradiation may be a promising process for the degradation of organophosphorus pesticides.

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