

Determination of Toxic Products Released during Combustion of Selected Pyrethroids

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Synthetic pyrethroids are widely used for pest control in modern industrial agriculture. These substances largely replace pesticides, which are being withdrawn. However, wide use of pyrethroids results in production, storage and distribution of those chemicals posing other hazards for human and the environment than pest control.

Unwanted combustion during incidents, accidents or major accidents may lead to formation of more dangerous substances than those involved in an emergency event. Dangerous gaseous substances released during fire are a threat not only to employees of industrial plants and warehouses, where the incident occurred, but also to firefighters, people involved in rescue operations and local residents. Therefore, knowing what toxic substances may be formed as a result of a fire is significant for an analysis and risk management of production processes, storage and distribution of those pesticides.

In this paper, the thermal degradation of three representatives of pyrethroids: beta-cyfluthrin, deltamethrin and lambda-cyhalothrin were studied. In the first stage of research the Simultaneous Thermal Analysis (STA) that combines thermogravimetry (TG) and differential scanning calorimetry (DSC) was used to determine thermal characteristics of pyrethroids, e.g. the relation between mass loss and temperature (TG), melting temperature and initial decomposition temperature. The second stage was for identification of gaseous combustion products. Also a Purser furnace was used to heat the substances and made it possible to identify substances formed during side reactions of combustion of the pyrethroids. Newly-formed substances were identified with an infrared spectroscope with Fourier transformation (with on-line connection) and, additionally, with a gas chromatograph with mass spectrometry.

The obtained results led to conclusion that the major compounds identified in the gaseous products were organic compounds, polycyclic aromatic hydrocarbons and halogenated aromatic hydrocarbons, which all are carcinogenic and mutagenic pollutants.

1. Introduction

Pesticides are widely used in both agricultural and industrial applications. They are employed to control and eliminate pests that threaten agricultural production, spread diseases and cause material damage. Unfortunately, in spite of their benefits, pesticides pose a potential threat to people and to the environment.

Thermal decomposition and combustion of pesticides can occur in different situations. First of all during the processing of vegetables and foods poisoned by traces of pesticides (Holden et al., 2001, Juhler, 1998, Senneca et al., 2007). Large amounts of hazardous substances such as pesticides are handled and stored every day in chemical plants and warehouses as a consequence of their massive use in the agricultural field (Andreozzi et al., 1999, Senneca et al., 2007). It has been reported in the past that fire occurred in a certain number of these both installations involving large quantities of chemicals (Christiansen, 1994). Toxicity, thermal instability and reactivity of pesticides caused several accidents during not only the storage of chemicals but also during the production and transport (Cozzani et al., 1998, Koller et al., 2000, Sanchirico et al., 2012). Another possibility of release of toxic species into the environment is the incorrect method of disposal of agricultural waste, for example burning of empty pesticide containers in open fires (Damalas et al., 2008).

The products released during thermal decomposition and combustion of pesticides can cause serious air pollution, harmful not only to firefighters but also to people living in the surrounding area (Smith-Hansen and Jogensen, 1993). Moreover, water used by fire fighting, mixed with these toxic products can contaminate the surface and ground water and cause major environmental pollution affecting the ecosystems (Atkinson and Jagger, 1992).

The Seveso accident (Wood, 2009), which gave the name to the European Directive on the control of major accident hazards involving dangerous substances (EU, 2012), is a well known example of the very severe hazards that may derive from major accident. Several studies proposed methods for the identification of possible unwanted products formed in "out of control" conditions, mainly starting from past accident analysis, from the definition of experimental protocols and from simple predictive methodologies (Andreozzi et al., 2008, Barontini et al., 2008, Kersten et al., 2003, Lunghi et al., 2004, Marsanich et al., 2004, Sovizi and Anbaz, 2010). However, in spite of the relevant work carried out to develop and standardize experimental protocols and predictive methods, insufficient data are often available on the decomposition products that may be formed due to the thermal degradation or partial combustion of chemicals (Sanchirico et al., 2012). Hazardous substances formed during unwanted combustion of pyrethroids can be identified with various analytic methods (Chen et al., 2012).

In this study the representatives of pyrethroids: beta-cyfluthrin, deltamethrin and lambda-cyhalothrin were studied. The first stage of research consisted in determining stability and thermal decomposition. Simultaneous Thermal Analysis (STA) was used to determine thermal characteristics of pyrethroids, e.g. the relation between mass loss and temperature, melting temperature and initial decomposition temperature. The second stage involved identifying gaseous combustion products during temperature increase and for temperatures selected in STA. Moreover the steady state tube furnace (Purser et al., 2013, ISO/TS 19700, 2007) has been used especially to generate toxic products from the real fires under different temperature conditions. The released species have been identified using an infrared spectroscope with Fourier transformation (FT-IR) (with on-line connection) and, additionally, a gas chromatograph with mass spectrometry (GC-MS). The solid phase microextraction (SPME) was used as a technique which combines sampling and concentrating analytes as well as introducing them to the chromatographic system (Mark and Sandercock, 2008). In the paper comprehensive studies of substance identification that can be formed during combustion of selected pyrethroids in different conditions are presented. The SPME technique allows identifying a wide range of organic compounds formed during the thermal degradation of the selected pyrethroids. The carboxen/polydimethylsiloxane (CAR/PDMS) fiber coatings were used because they are recommended to the extraction of non-polar and polar analytes (Fumes et al., 2015). Moreover they were used during analysis of pyrethroid residuals (Li et al., 2009).

2. Methodology

The beta-cyfluthrin, deltamethrin and lambda-cyhalothrin (99.4 % purity, certificated analytical standard) were supplied by the Institute of Industrial Organic Chemistry (Poland). The pyrethroids (> 92% purity) used in the Purser furnace study were obtained from Haihang Industry Co., Ltd. (China).

Thermal decomposition of selected pyrethroids was studied in air atmosphere using a simultaneous thermal analyzer (STA 449F3 Jupiter, Netzsch, Germany). The 20 mg samples were placed in aluminium oxide crucibles and heated at a rate of 10 °C min⁻¹ from room temperature (25 °C) to 900 °C. The flow rate of the air was 30 ml min⁻¹ and the nitrogen was 20 ml min⁻¹. The volatile products evolved during thermal decomposition were analyzed by Fourier-transform infrared (FT-IR) spectrometer (Tensor 27, Bruker, Germany) coupled on-line to the STA instrument. The gas cell of FT-IR and transfer line were maintained at 200 °C. The spectra were recorded in the spectral range of 650 – 4000 cm⁻¹ with 16 scans per spectrum at a resolution of 4 cm⁻¹.

The thermal decomposition and combustion of selected pyrethroids was investigated in the steady state tube furnace (Purser furnace) too. The samples of selected chemicals (about 15 g) were delivered into a furnace tube set at 500 °C. After 15 min the samples of effluents were taken from the mixing chamber by introducing the SPME device with a carboxen/polydimethylsiloxane fibers (Supelco, USA) to sampling ports. Before the use the fibers were conditioned in the injection port, according to the manufacturer's instructions. After introducing the SPME syringe to mixing chamber, the gaseous products of thermal decomposition of pyrethroids were sorbed on the SPME fiber. After collection (10 min), the SPME fiber was withdrawn from the chamber and desorbed immediately in the gas chromatograph injector for analysis. The gaseous products were detected by gas chromatograph (7890 A, Agilent Technologies, USA) with mass selective detector (MSD 5975, Agilent Technologies, USA). The detector was operated in the electron ionization (EI) mode (70 eV). The temperatures for the interface, MS source and MS quad were set at 220, 200 and 150 °C, respectively. During the measurements m/z ratio was recorded in the range 30 – 260 amu. Separations were performed with the aid of gas chromatography (GC) on an HP-5 MS fused silica capillary column (30 m × 250 μm × 0.25

μm film thickness) from Agilent Technologies (USA) using helium as a carrier gas. The GC oven program was established as follows: 40 °C hold for 10 min; 5 °C min^{-1} ramp to 100 °C hold for 25 min; 5 °C min^{-1} ramp to 200 °C; 20 °C min^{-1} ramp to 280 °C hold for 10 min. The temperature for the front inlet was set at 280 °C. The gaseous products were identified using the GC-MS database and in the NIST database.

3. Results

The results of thermal degradation of the beta-cyfluthrin, deltamethrin and lambda-cyhalothrin performed under air atmosphere are shown in Figure 1. The beta-cyfluthrin is an enriched isomeric form of the two biologically active diastereoisomeric pairs of isomers of cyfluthrin, so it start melting at 74.5 °C, during two endothermic process. The second selected substance - deltamethrin - melts at 95.3 °C. The lambda-cyhalothrin starts melting at lower temperature (~ 45.9 °C) during the endothermic process. For all tested substance the weight losses were between 250 and 700 °C in two stages. However, at the first stage the weight loss was about $\sim 80\%$ for beta-cyfluthrin and deltamethrin, and $\sim 90\%$ for lambda-cyhalothrin.

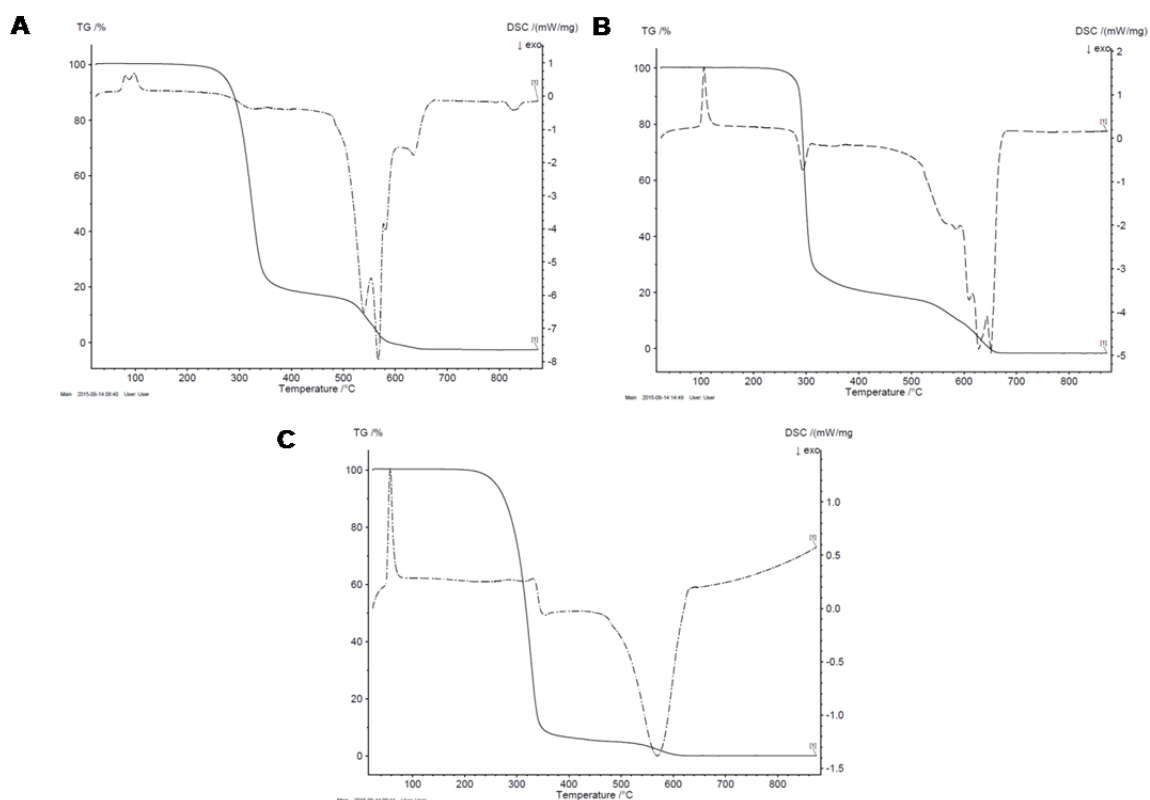


Figure 1: TG and DSC curves of the thermal decomposition of beta-cyfluthrin (A), deltamethrin (B) and lambda-cyhalothrin (C) in air atmosphere. The heating rate equals 10 °C min^{-1} and the amounts of selected pyrethroids were 20 mg.

Figure 2 presents the 3D IR spectrum of gases emitted from the sample during the degradation process. The application of online FT-IR system allows to notice that the concentration of all gaseous components in the samples were changing with temperature (time) of the experiment. Moreover the temperature and intensity of the emitted gas products depends on the type of compound. The results obtained from TG/DSC curves show that at 500 °C there is significant degradation of selected pyrethroids accompanied by the emission of volatile products. Therefore, this temperature was selected for Purser furnace experiments. Examples of selected spectra obtained in 500 °C are shown in Figure 3. The main emitted compounds were carbon oxides, water and other organic substances.

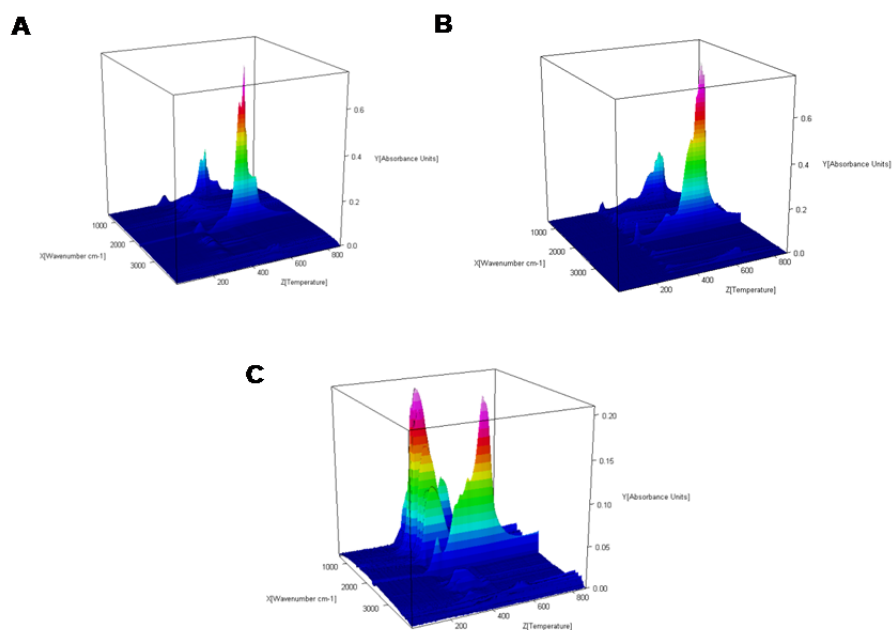


Figure 2: 3-D infrared spectrum of evolution gases during thermal decomposition of beta-cyfluthrin (A), deltamethrin (B) and lambda-cyhalothrin (C) in air atmosphere.

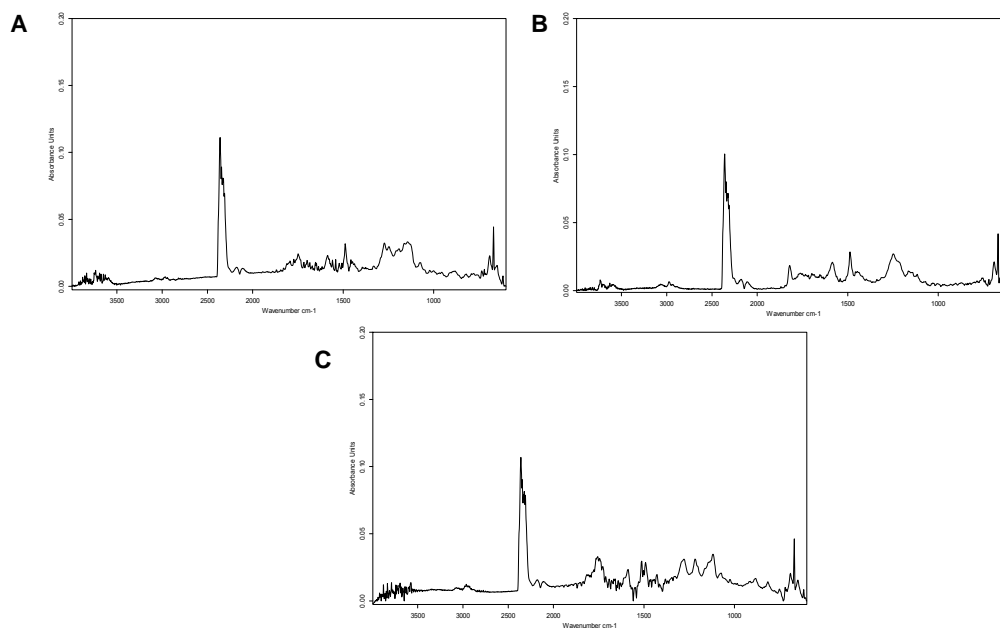


Figure 3: Selected FT-IR spectra for the volatile components emitted during thermal decomposition of beta-cyfluthrin (A), deltamethrin (B) and lambda-cyhalothrin (C) in air atmosphere.

Gas chromatography data of the gas samples released from selected pyrethroids during thermal decomposition at 500 °C are shown in Figure 4. The probable main components were identified using the GC-MS database and the NIST database. During combustion of beta-cyfluthrin the compounds such as: 1-chloro-3-methyl-benzene; 4-methyl-benzonitrile; 4-fluoro-benzeneacetonitrile; 6-hydroxy--methyl-2-phenyl-1-H-pyrazolo [3,4-b] pyridine-3(2H)-one, 3-(5-formyl-2-furyl)-benzoic acid, 4-fluorodiphenyl ether and diisopropylamine were identified. Whereas during thermal degradation of deltamethrin in gaseous products were compounds such as: 2-methyl benzoic acid; diphenyl ether; 1-bromo-4-(1-methylethyl) benzene; 1-

methyl,3-phenoxy-benzene; 2-bromo-4-t-ocylphenol; 3-phenoxy benzaldehyde and 1-amino-9,10-anthracenedione. The gaseous products emitted during thermal degradation of lambda-cyhalothrin contained: trifluoromethyl benzene; 2-(trifluoromethyl) benzenethanol; chlorobenzene; styrene; benzonitrile; naphthalene; diphenyl ether; biphenyl; 1-methyl-3-phenoxy benzene and 3-phenoxy benzaldehyde.

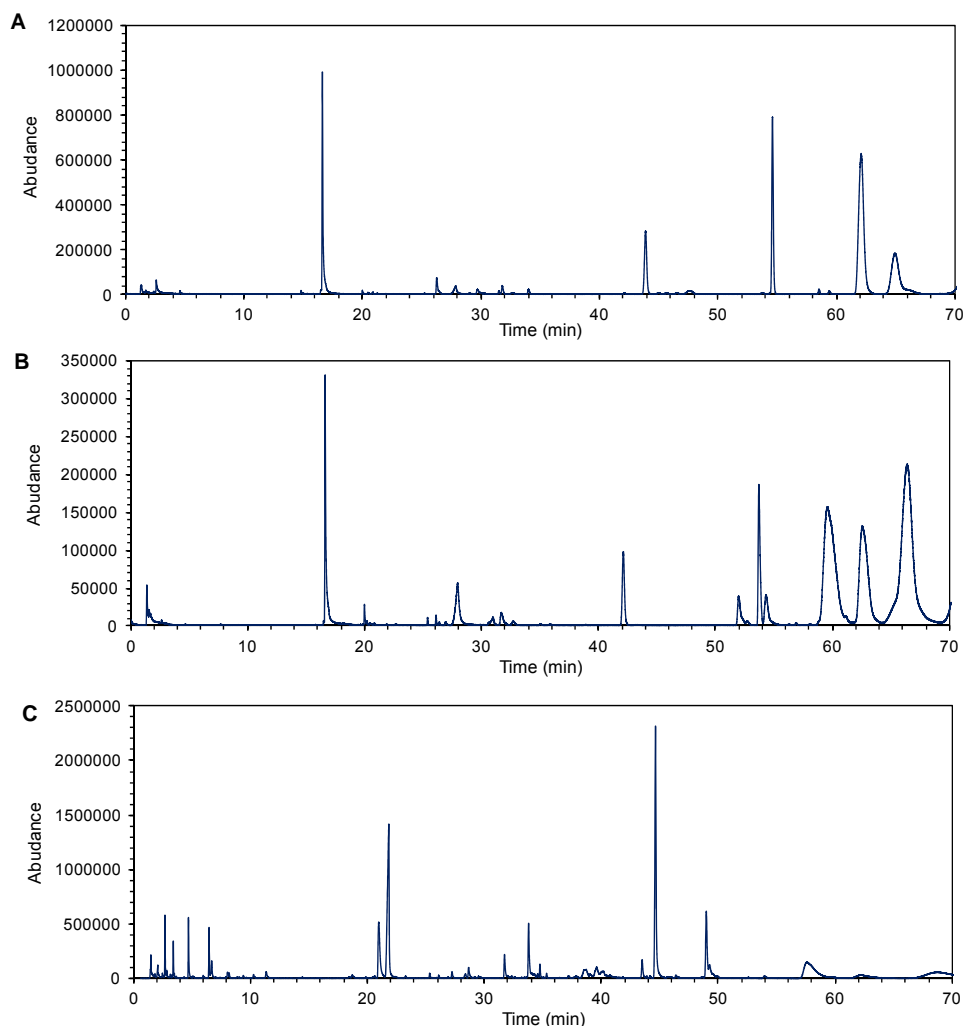


Figure 4: Chromatograms of gas products emitted during thermal degradation of beta-cyfluthrin (A), deltamethrin (B) and lambda-cyhalothrin (C) in air atmosphere at 500 °C.

4. Conclusions

Thermal degradation process of selected pyrethroids can be divided into two stages: thermal degradation and oxidation. The concentration and type of volatile products released during combustion of beta-cyfluthrin, deltamethrin and lambda-cyhalothrin strongly depended on the temperature of the reaction. Generally, chemical reactions occurring during thermal degradation process of chemicals involve fragmentation of the molecules of the compounds and other subsequent reactions. The major compounds identified in the gaseous products were organic compounds, polycyclic aromatic hydrocarbons and halogenated aromatic hydrocarbons. Most of these substances have been identified as carcinogenic and mutagenic (as well as teratogenic), and are considered as pollutants.

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