Gas Chromatography - Mass Spectrometry

Lourdes Berdié[1], Irene Fernández[2], and Pilar Teixidor[1]

[1] Unitat de Cromatografia de Gasos i Espectrometria de Masses, CCiTUB. Lluís Solé i Sabarís 1-3. 08028 Barcelona, Spain.

[2] Unitat d'Espectrometria de Masses (Química), CCiTUB. Facultat de Química. Martí i Franquès s/n. 08028 Barcelona, Spain

email: *lourdesb@ccit.ub.edu, i.fernandez@ccit.ub.edu, teixidor@ccit.ub.edu*

Abstract. This article briefly describes the possible configurations of the gas chromatography- mass spectrometry (GC/MS) technology available at the CCiTUB. Some developed examples of different applications are shown.

1. Introduction

The technology of gas chromatography-mass spectrometry (GC/MS) combines the fine separating power of GC (complex mixtures of hundredths of compounds) with the two main competences of MS:

- Powerful detection
- Strong capacity of unknown identification

The applied GC/MS unit of the Scientific and Technological Centers has the ability to select, practice and develop the different appropriated methods of extraction, clean-up, concentration and derivatization of organic compounds in a great variety of natural and synthetic samples, from mineral to biological world in order to analyze the prepared extracts by GC/MS towards the process of identifying and quantifying the extracted organic compounds.

Method developments and subsequent validation following the International Conference of Harmonization (ICH) guidelines are also performed if they are required.

2. Methodology

Several GC/MS systems with capillary column separation and different ionization methods are available in the Unit. These systems are summarized in Table 1.

Table 1. Summary of the different GC/MS systems available at the CCiTUB

Ionization method	**Analyzer**	
Electron ionization (EI)	Quadrupol Mass Filter	IonTrap Quadrupol
Positive chemical ionization (PCI)	Quadrupol Mass Filter	
Negative chem. ion. (NCI)	Quadrupol Mass Filter	

The detection in the Quadrupol mass filter MS instruments can be performed in scan or single-ion monitoring (SIM) mode. In the scan mode, a specified mass range is scanned at regular intervals during the chromatographic process and stored in the data system. This mode provides reproducible mass fragmentation patterns that originate the mass spectra. With this information it is often possible to identify the GC separated unknown compounds. There are some spectral databases (commercial libraries) that assist the analyst in the process of identification. In spite of this, experienced analysts are required and considerable care must be exercised in interpreting the results of such comparisons. The identifying process can be assisted by the additional measurement of the retention index for each peak eluted and quantification is also possible by integration of the different ion peaks present in the chromatogram using internal and/or external standards.

With the MS^n ability of the ion trap analyzer, the possibility to detect an unknown in a complex mixture is enhanced and this tandem mode also provides additional structural information to help in the identifying process.

According to the nature of the sample and the volatility of compounds to be analyzed, some different sample introduction systems can be applied:

- Static Head Space (HS)
- Solid phase microextraction (SPME)
- Thermal desorption (TD)
- Direct liquid/gas injection

A summary of the different sample introduction systems used for volatile and semivolatile compounds is given in Table 2.

Table 2. Summary of the different sample introduction systems for volatile (VOC) and semivolative (SVOCs) compounds

Compound	**Sampling**			
VOCs	HS	TD	SPME	Direct
SVOCs	Direct		SPME	

Volatile compounds (VOCs): This group includes low-molecular weight compounds (ca < 250 uma) with high-vapour pressures and low-to-medium water solubilities. Some of them have natural origin but the majority is anthropogenic, which are used and produced in the manufacture of cleansers, paints, adhesives, plastics, pharmaceuticals, refrigerants, etc. They often are compounds of fuels, solvents, lubricants, paint thinners and dry-cleaning agents commonly used in urban settings. Most of them cause environmental problems and are potential carcinogens, and therefore, their control becomes obligatory and regulated.

Semivolatile compounds (SVOCs): There are organic compounds with molecular weights up 1000 amu, which may vaporize when exposed to temperatures above room temperature (usually with a boiling point >100ºC). In this group, some compounds such as common pesticides (OC's, OP's, triazines), persistent pollutants (phthalates, nonylphenols, PCBs, PAHs), neutral lipids, small metabolites, aliphatic and aromatic hydrocarbons, fragrances, essential oils and relatively non-polar drugs are analyzed in different matrices. In order to increase the volatility of compounds containing polar functional groups (-OH, -COOH, $-NH_2$, etc.), chemical derivatizations, e.g. silyl derivatives for alcohols and amines, methyl esters, transterification, are often employed in order to extend the range of suitable analytes to such compounds as steroids, polar drugs, polar lipids, organic acids, and aminoacids.

3. Examples of applications

3.1. Authentication analysis of personnel care products

In order to detect differences between two similar commercial deodorant spray samples (original branded and imitation), the analysis of volatile organic compounds was performed. The obtained results revealed multiple coincident compounds in both samples but the synthetic musk galaxolide (1,3,4,6,7,8-Hexahydro-4-6-6-7-8-8-hexamethyl cyclopenta-[g]-2-benzopyran) was only detected in the original spray. However, in the imitation sample, high amount of ethanol was found and floropal (2,4,6-Trimethyl-4-phenyl-1,3-dioxane) was detected instead of the polycyclic musk. The GC/MS ability to filter specific ions permitted to detect this 1,3-dioxane odorant which coeluted with a menthol derivative. The different chromatograms and mass spectra obtained in this example are shown in Figs. 1-5.

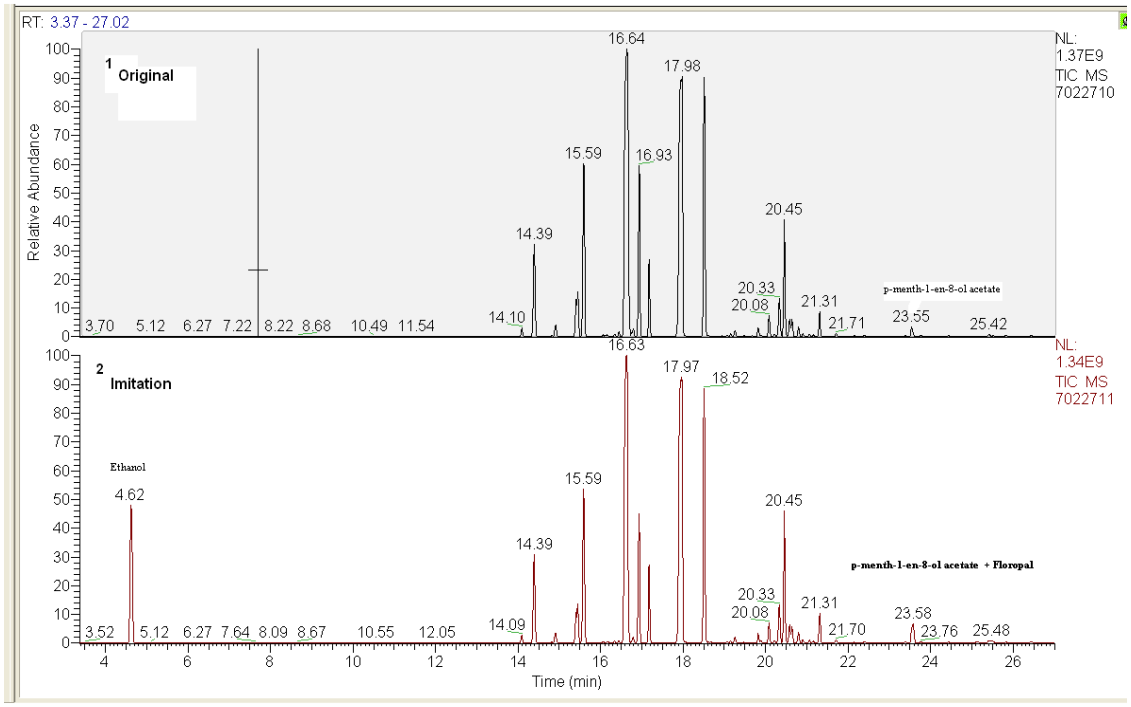

Figure 1. Comparison of the chromatograms corresponding to the original and defective samples obtained by HS-GC/MS on a DB-624 column. Note: Coelution between p-menth-1-en-8-ol acetate and floropal (only in sample 2).

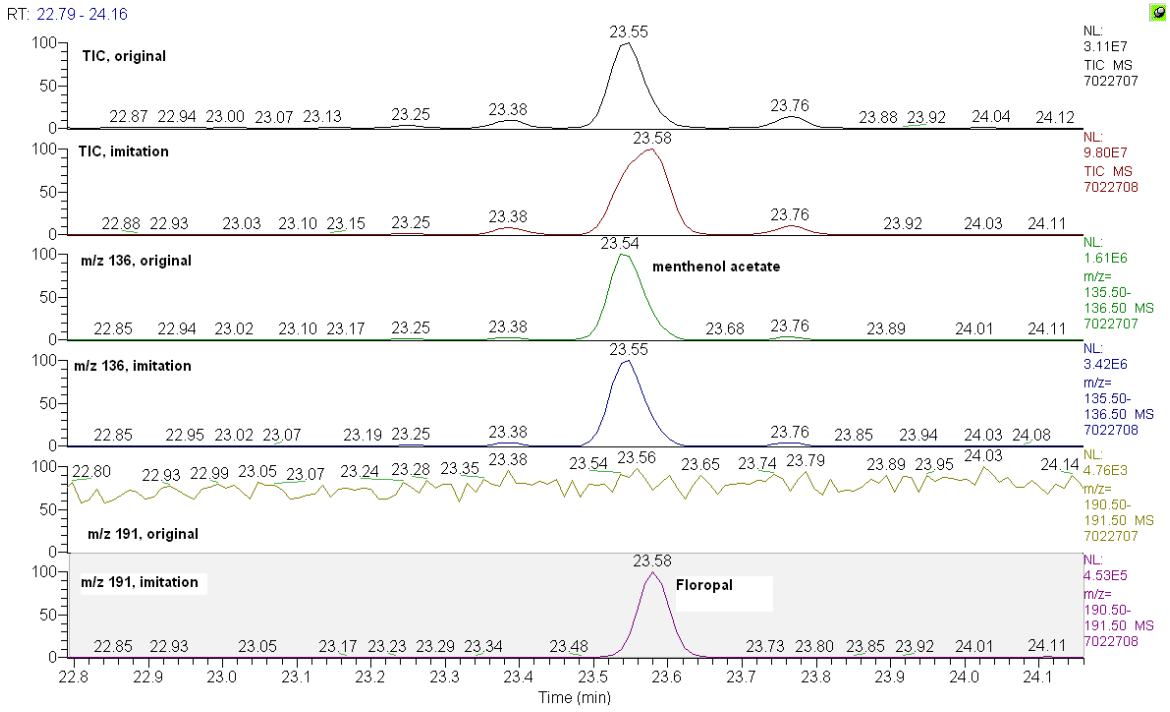

Figure 2. Mass chromatograms corresponding to the original and defective samples. Trace ions m/z 136 corresponding to p-menth-1-en-8-ol acetate and m/z 191 to floropal

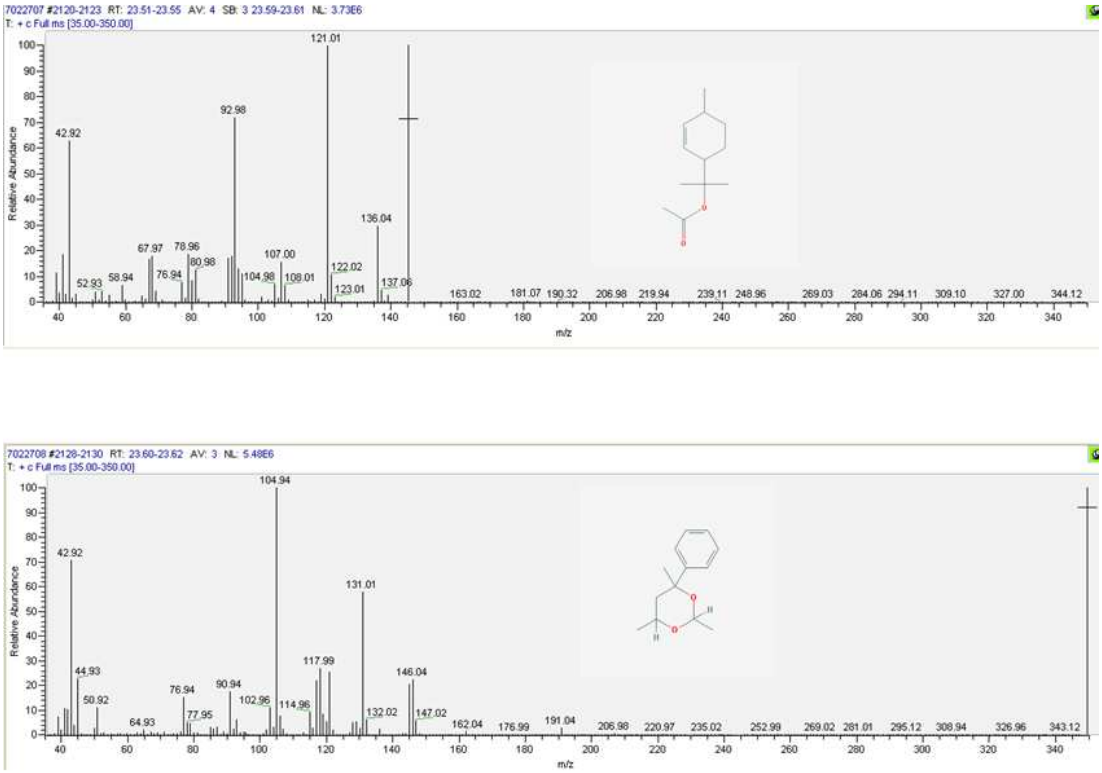

Figure 3. Mass spectra of p-menth-1-en-8-ol acetate (top) and floropal (bottom)

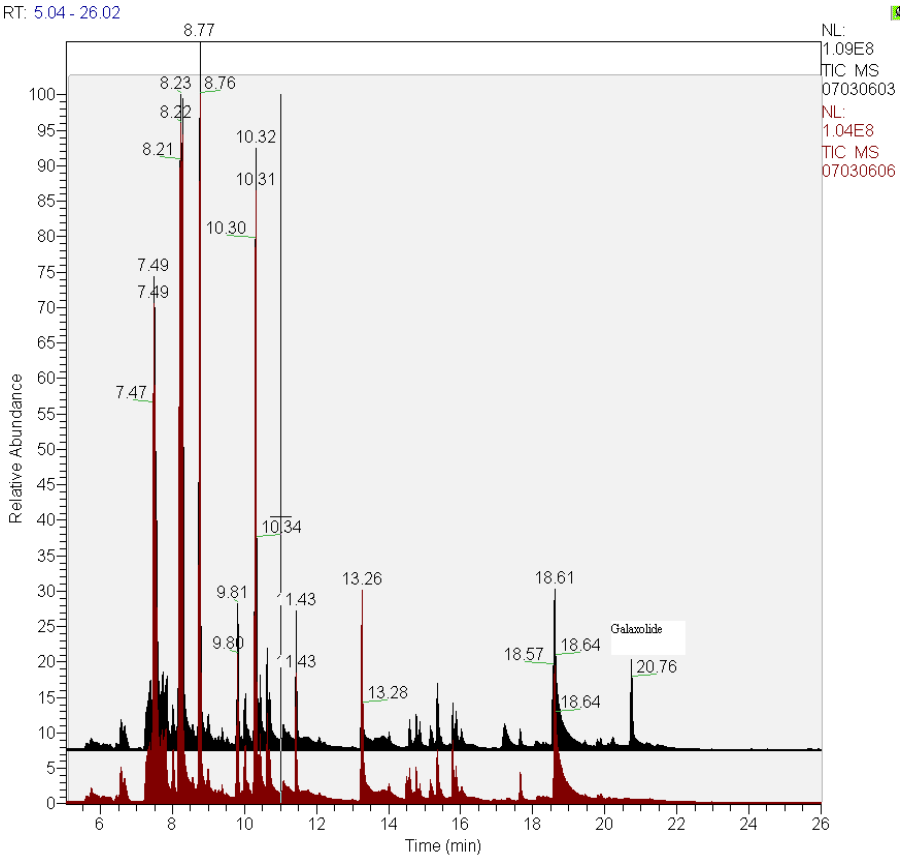

Figure 4. Comparison of the chromatographic profiles corresponding to the original and defective samples obtained by GC/MS on a VF-5MS column.

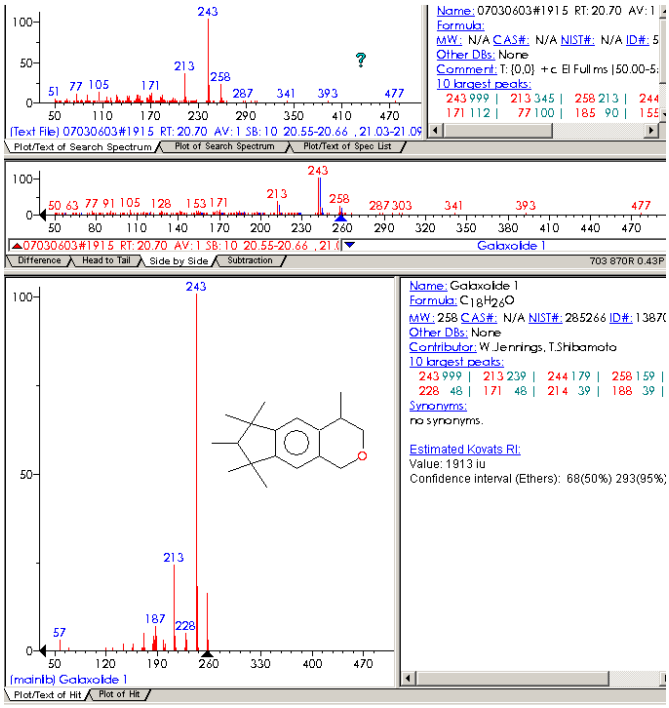

Figure 5. Mass spectrum of galaxolide with the corresponding library search result.

The original deodorant could be distinguished from the copy with the GC-MS technique. Even in the case of a coelution, it was possible to find differences between both samples.

3.2. Odour markers in food containers

In order to detect some odour markers in defective tin containers, samples were analyzed by head-space gas-chromatography mass spectrometry (HS-GC/MS). The VOCs chromatograms revealed some significant quantitative differences between a blank sample (correct) and an odorant sample (defective). In the latter sample, higher concentrations of chlorinated compounds and phenol were detected. These compounds could be responsible for the unpleasant odour (see Fig. 6)

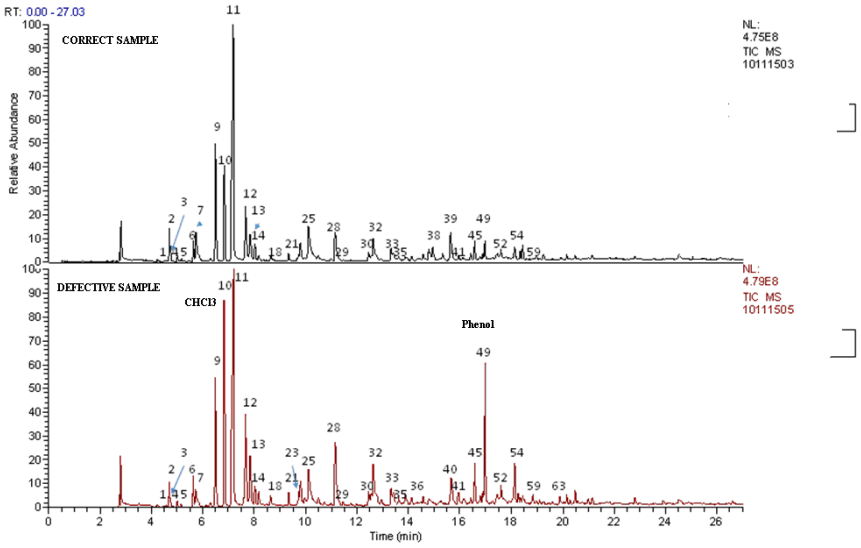

Figure 6. Comparison of the chromatographic profiles corresponding to the original and defective samples obtained by HS-GC/MS on a DB-624 column

3.3. Biomarkers in archaeological residues

Lipid biomarkers extraction and analysis of cooking wares residues (5th century AD) from Sa Mesquida (Mallorca, Spain) were performed by GC/MS. The origin of food contained in the archaeological ceramics could be distinguished from the fatty acids profile (Pecci) .

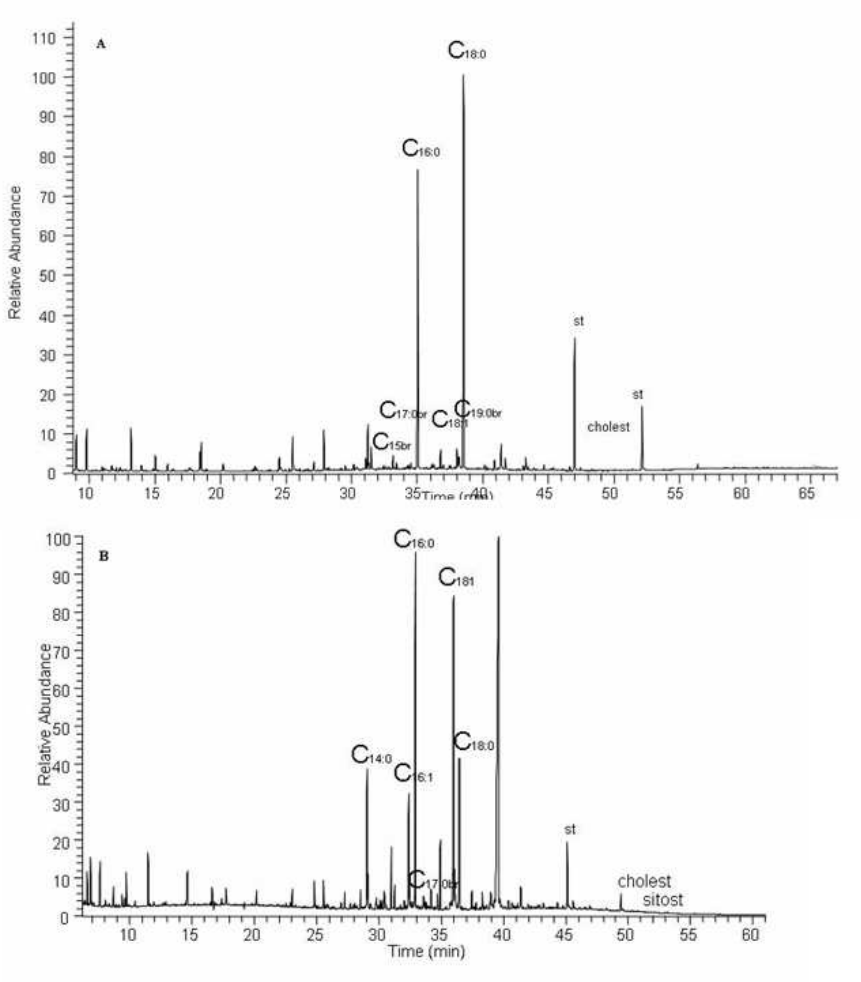

Figure 7. Chromatograms corresponding to a different total lipid extract samples. The fatty acids profile in sample A, where the saturated acids are clearly dominant, suggests an animal fat trace. In contrast, the fatty acids pattern showed in sample B suggests that a vegetal fat origin as unsaturated acids is relevant.

3.4. Determination of fenthion in liver samples (GC/MS^n example)

Fenthion is an organophosphorous (OPs) pesticide of regulatory concern for health and safety problems due to its lipophilic properties and large degree of persistence in the environment. One of the most important organophosphorous compounds reactions is water hydrolysis. Moreover, OPs inhibit the phosphorylate esterases, particularly the enzyme acetylcholinestarase, thus causing an accumulation of the neurotransmitter acetylcoline. Other effects are mutagenicity and carcinogenicity as well as specific organ toxicity to heart, liver, kidney and other organs.

For this compound, extraction and clean-up procedures are long and generally involve several steps (e.g. extraction, GPC and SPE clean-up), which can imply systematic losses and consequent inaccuracy (Russo et al., 2002). Ion trap tandem mass spectrometry is a useful approach to reduce clean-up steps in such a complex matrix. Using this technique, analysis of fenthion in liver samples can be achieved with a simple extraction (Figs. 8-11)

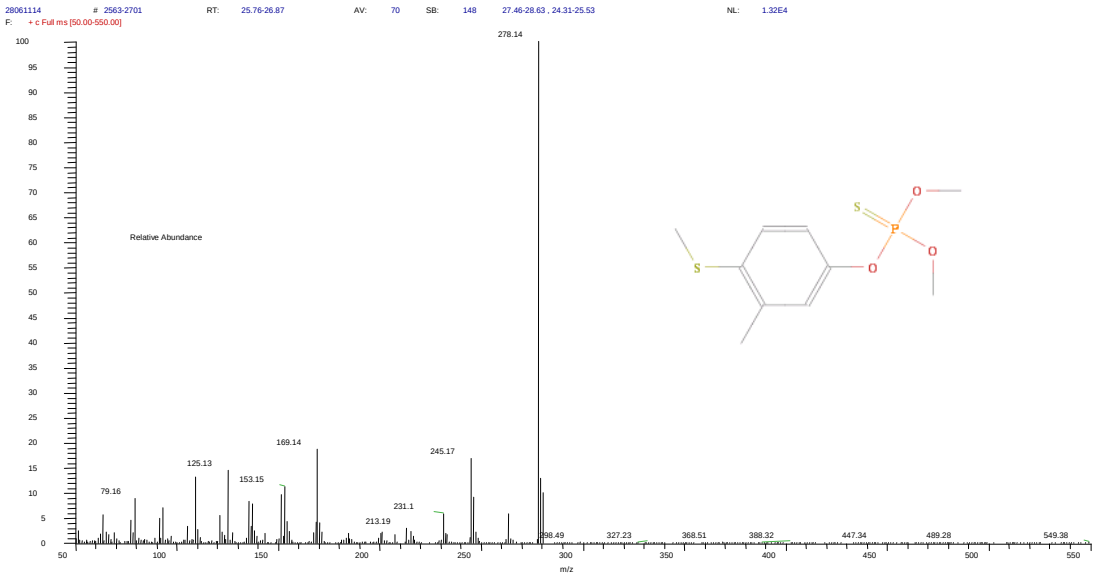

Figure 8. Fenthion mass spectrum (EI) obtained in an ion trap analyzer from a 2 ppm standard solution

In a liver sample, a coelution at 25.98 min is observed due to palmitic acid present in the liver.

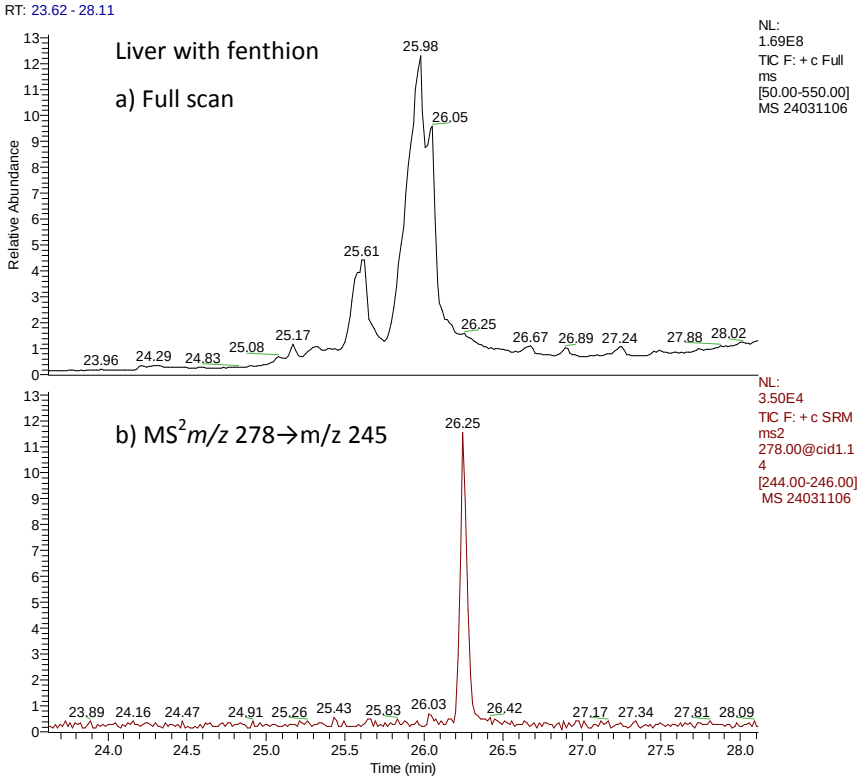

Figure 9. Liver extract zoom chromatogram. a) TIC chromatogram and b) SRM 278 to 245 amu

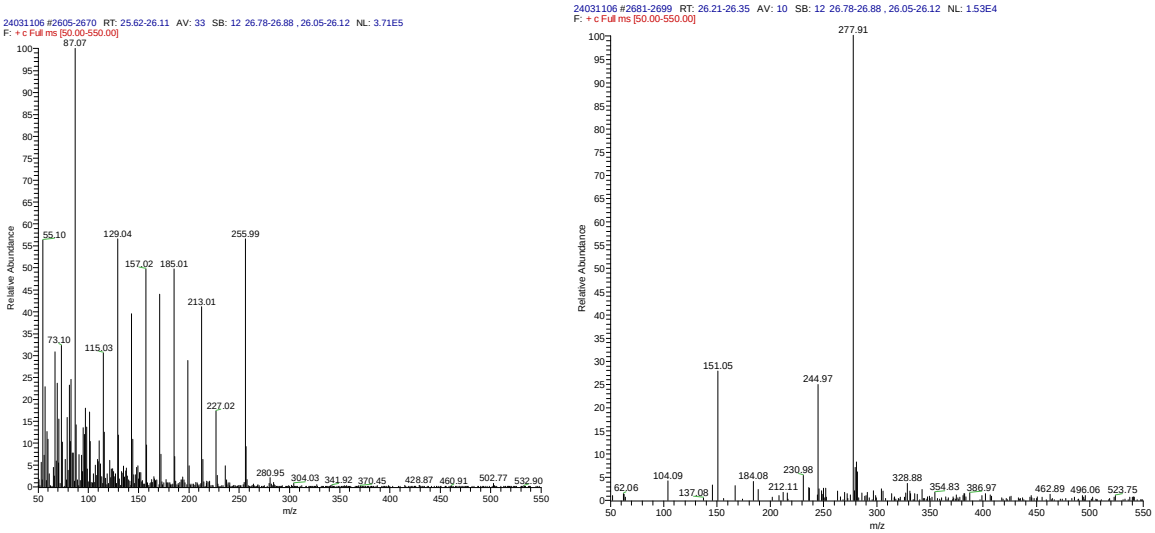

Figure 10. Mass spectra of palmitic acid (left) and fenthion (right) in liver extract.

Signal to noise ratio observed for SRM from 278 to 245 amu is better than that observed for the 278 mass chromatogram.

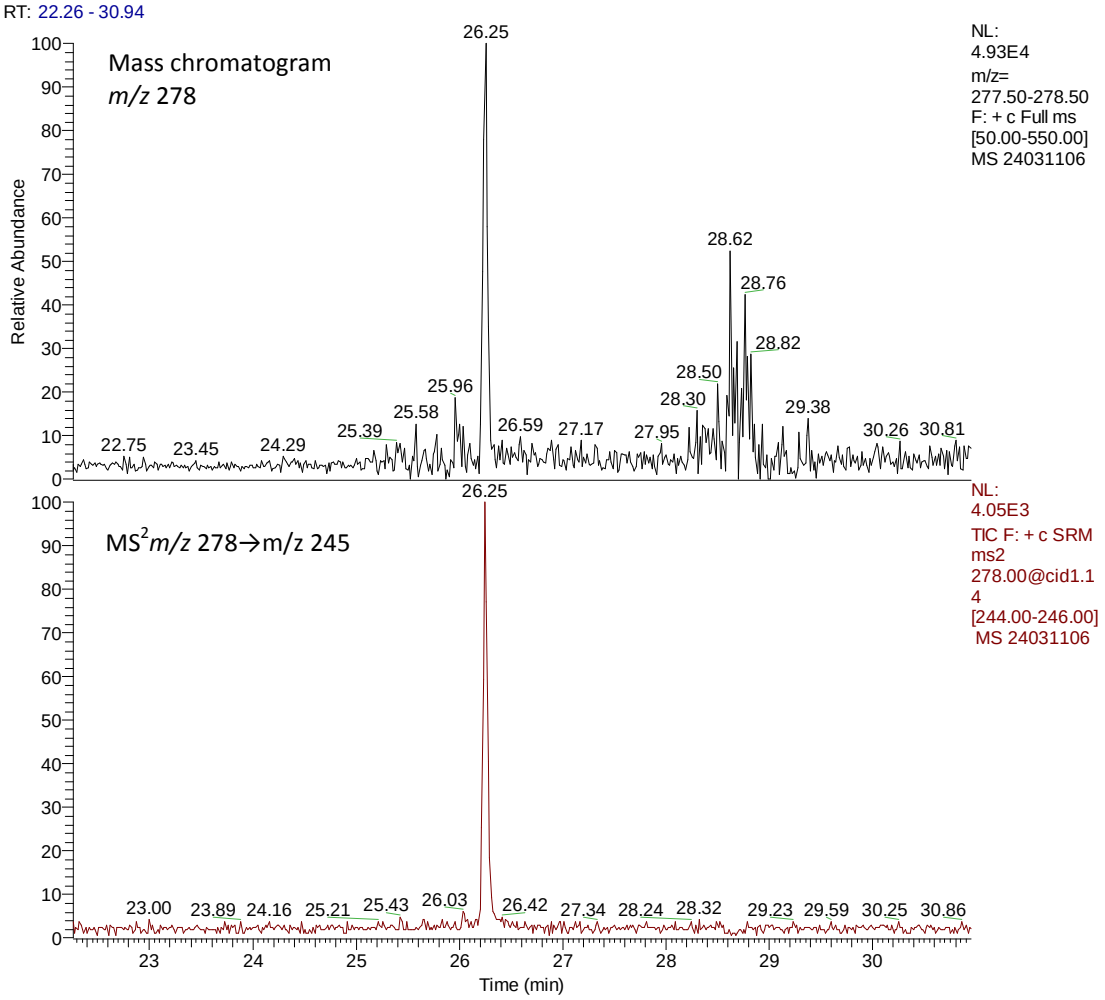

Figure 11. Mass chromatogram m/z 278 and SRM from 278 to 245 amu.

3.5. GC-MS Structural Characterization of polyesters produced from Linseed Oil by *P. aeruginosa 42A2*

Poly[3-hydroxyalcanoates] (PHAs) are optically active polyesters. The PHA synthesized by numerous bacteria are high-molecular weight polymers which form intracellular inclusion bodies such as carbon and energy reservoir. These polymers are environmentally friendly, biodegradable and may become an alternative for biocompatible materials. The native polymer has a random composition of monomers ranging from C6 to C14 with 20% of the alkyl side chains exhibiting unsaturation at C12 and C14 alkyl side chains. A strategy for the study of the nature of these PHA by GC/MS has been developed in our Unit. Biodegradable polymer was extracted from lyophily zed cells with $CHCl_3$ and after purification (MeOH precipitation) was hydrolyzed ($CHCl_3$, H_2SO_4, MeOH, 100C, 3h) in order to obtain the monomers (3-hydroxy-methylesters). The monomers were silylated and characterized by GC-MS (see Figs. 12-14).

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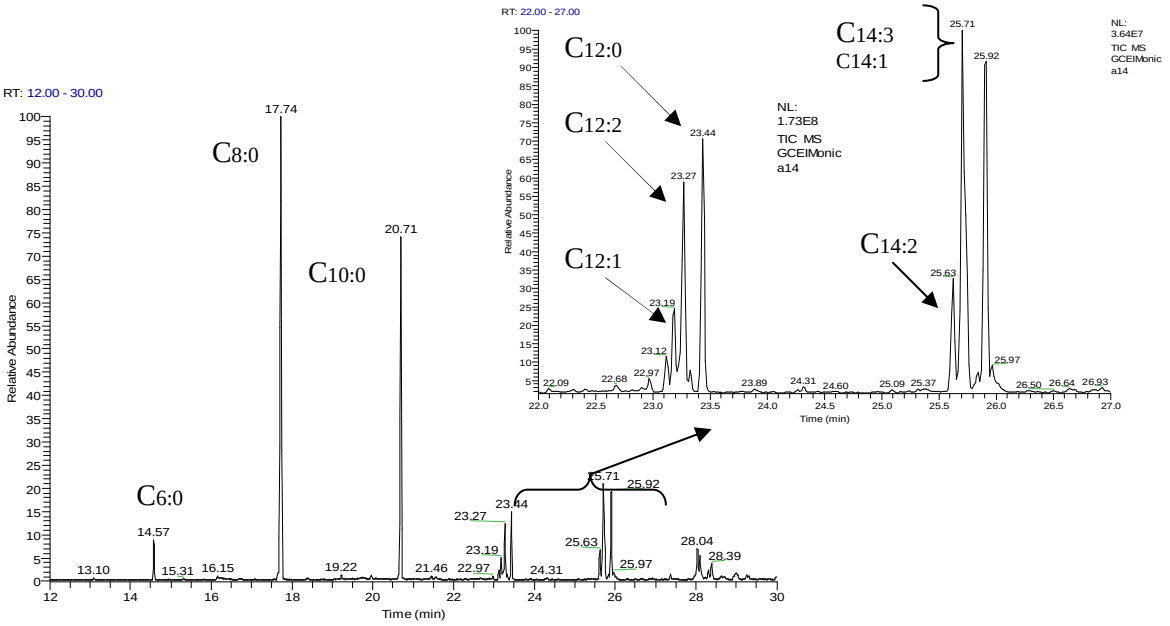
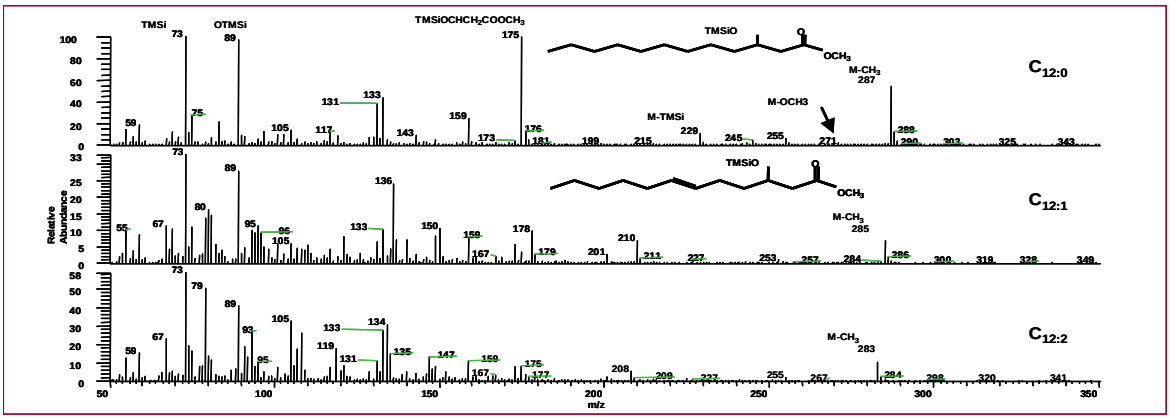
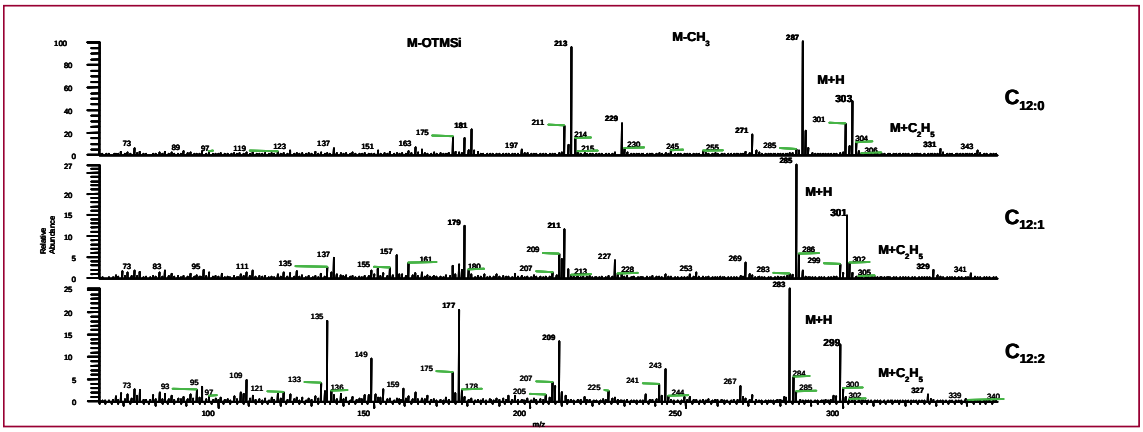


Figure 11. Ion Chromatogram (TIC) of the trimethylsilyl derivatives of (3-hydroxy-methyl esters) monomers.



. **EI** mass spectra correspondig to the C_{12} family

Figure 12. EI mass spectra corresponding to the C_{12} family



CI (CH_4) mass spectra correspondig to the $C_{12:0}$ monomers.

Figure 13. CI (CH_4) mass spectra corresponding to C_{120} monomers

Acknowledgements

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References

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A. Pecci (ERAA-UB), IEF-FP7 Profolant Marie Curie Project

Russo et al., 2002 Journal of Chromatography B, 780:431-434