DEVELOPEMENT OF ANALYTICAL TECHNIQUE FOR THE DETERMINATION OF PESTICIDES RESIDUES FROM FOOD

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The quality of food influences the life quality and health of the consumer. In the battle for survival between humans and insects, the use of pesticides in our foods supply has become nearly universal. Many people are concerned about the potential hazards they and their children might encounter from eating produce that contains levels of pesticides high enough to cause harm. The presence of pesticides in aliments harms the nervous system, the cardiovascular apparatus, decreases the immunity of human body. In addition, to ensure the foods quality and safety is a requirement, which must be fulfilled for the integration in U.E.

A gas-chromatograph (Varian 3800) coupled with a mass-spectrometer (Saturn 2100T)[1)] is used for quantitative and qualitative analysis of organochlorine and organophosphorous traces of pesticides.

Successful GC/MS applications imply special requirements for the GC:

- sample introduction must be accurate, precise and free of mass discrimination;
- the flow and thermal precision guarantee highly reproducible retention times.

Ion trap technology is referenced in current US EPA methods from volatiles to semi-volatiles and from water to air and waste. Detection limits are very low, of the order of ppm and ppb. The separation method requires the presence of compounds in gaseous phase, their boiling point must be less than 300 ^{0}C; the boiling point of a series of organic compounds with comparable molecular weight increases with increasing polarity of the compound. The success of the separation depends on the choice of the stationary phase with suitable polarity.

The subject of these paper is the presentation the results of tests and complementary studies for organochlorine and organophosphorous residues in food, particularly in wine and drinking water samples.

1. Steps in analytical technique for the determination of pesticides residues from food

1.1. Extraction of pesticides residues from samples matrix

For traces pesticides determination by GC/MS it is necessary a preliminary separation of pesticides from samples matrix. This separation is accomplished by a technique known as *extraction*[2)], where the organic compounds of interest are solubilized from a mixture of other substances. The pesticides can be extracted from a sediment sample by adding the solvent that will dissolve the organic compounds and leave the rest, making an extract consisting of organic residues (pesticides in petroleum ether in our examples) in a solvent. The choice of solvent is critical for the success of the experiment, it must dissolve as much of the desired compound as possible without dissolving other substances that might interfere with the analysis in a later step.

In our procedure we used the separatory funnel, traces of pesticides was retention in superior organic layer. Very important for safety of GC is to remove the water traces using sodium sulphate anhydrous. For wine, the next step is remove as many other organic substances as possible to minimize interferences in the GC analysis. This „cleanup" can be effected by passing the sample through a substance that will trap out many polar organic compounds, usually Florisil ($MgSiO_4$). Last stage is concentration of sample to the final volume using rotary evaporator.

1.2. Quantitative and qualitative analysis of pesticides residues of GC/MS data

Functional description: The main compounds are: Gas Chromatograph (GC), Mass Spectrometer (MS), Data System (DS) and AutoSampler (optional).

Fig.1. Varian Saturn 2100 GC/MS

A short [3)], line-of-sight transfer line (B) connects the GC and MS. The AutoSampler sits on the top of the GC. A fused silica capillary column (D) in the GC passes through the transfer line directly into the ion trap assembly (F). Samples are injected (C) either manually or via the AutoSampler onto the capillary column through the GC injection port. The gas chromatograph then separates the sample molecules. Effluent from the GC passes through the transfer line and into

the ion trap. The sample molecules next undergo electron or chemical ionization before being analyzed according to their mass-to-change ratios.

The ions are detected by an electron multiplier, which produces a signal proportional to the number of ions detected. The electron multiplier passes the ion current signal to the system electronics, which in turn amplify the signal, digitize the result, and pass it on the data system for further processing and display. The Varian turbo-molecular pump (A) is up and generates a high efficiency vacuum in mass spectrometer MS.

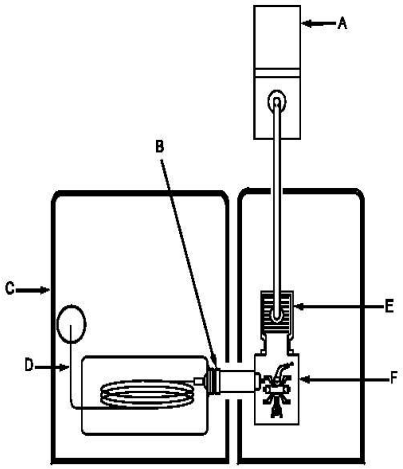

Fig.2. GC/MS coupling with ionic trap

The GC/MS analysis begins with injection of the sample into the instrument with a microseringe. The samples is first vaporised at high temperature (250-300 ^{0}C) in the injection port and then forced onto the separating capillary column by a carrier gas - helium - that serves as the mobile phase. For a successful analysis it is necessarry to choose the corect capillary column (is available a range of polimer coatings with varying polarities). In our experiments for pesticide traces analysis in wine and drinking water samples we chose the CP Sil 8 CB, non-polar chromatographic column. As the organic molecules pass through the column, they adsorb to the coating for varying periods of time depending on their structure and polarity. Each compound has a typical **retention time, R_t** that is dependent on the structure and polarity of the compound and the stationary phase. Temperature programming is useful for the separation of mixture of compounds that contain both low-boiling and high-boiling substances.

As the compounds elute from the end of the column, they flow through a detector where the concentration of each component in the mixture is measured as

a function of time, a plot of detector response versus time is called a chromatogram.

The topics in qualitative and quantitative analysis for pesticides residues are:

- Qualitative identification;
- Building a data handling method;
- Editing a data handling method;
- Building a recalculation list for calibration;
- Processing a recalculation list to add calibration data;
- Reviewing calibration results;
- Processing analysis files in a recalculation list;
- Reviewing analysis results.

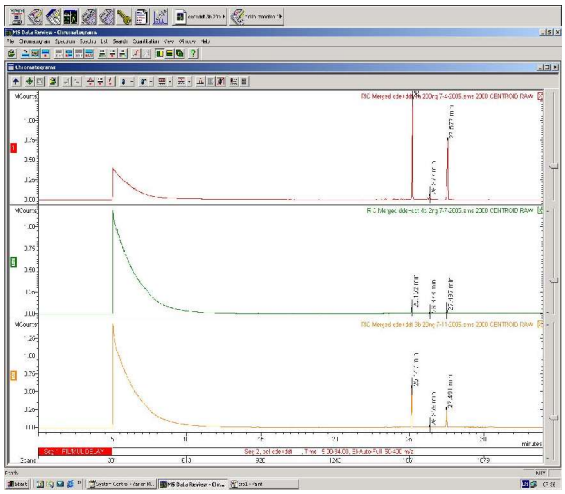

Fig.3. Pesticides residues chromatograms in different concentration in drinking water samples.

Fig.4. Tekmar Dohrmann Velocity Purge and Trap

Tekmar Dohrmann Velocity Purge and Trap

Velocity XTP device is used so that the water samples (water with organic volatile compounds) are injected directly without being necessary the extraction operations. The main condition imposed is that water should contain no mineral compounds.

Futures tendencies:

In the future, we intend to develop the sample preparation and chromatographic methods in order to realize the followings: analysis of organochloride and oganophosphorous pesticides in fruits and vegetable juices, animal and vegetal oils and fats etc.

Bibliography

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