Identification and measurement of pesticide contaminants in food products by electron impact GC/MS

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Abstract. The paper concern is determination of eight pesticides in food products samples. The target compounds are: Lindane, Heptachlor, Aldrin, o,p-DDE, Dieldrin, Endrin, p,p'-DDT, and Methoxychlor. The compounds quantities were performed from chromatographic area obtained in full scan GC/MS mode after baseline separation and by comparation with surrogate internal standard area (Diphenylamine). The samples were concentrated by extraction with organic solvents (acetone) by Solid-Liquid Extraction (SLE) procedures the recovery factors being better than 80% except for Heptachlors. The coefficient of correlation of detector response function was better than 0.913 and LOQ under 0.015 µg/g. The method enables to determine pesticides at low µg/g in food supplements.

1. Introduction

Pesticides comprise a large number of substances that belong to different chemical groups – the only common characteristic is that they are effective used against pests [1]. This class of compounds are widely used to combat diseases and pests, and may have main effect in the production of vegetable and animal foodstuff. By their large use residues of those compounds can reach the environmental compartments or human food [2, 3].

Most of the chemical compounds released into the environment via human activity are among the most dangerous chemicals. They are highly toxic, causing a number of adverse effects, notably death, diseases and birth defects between human and animals. Specific effect can include cancer, allergies and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system [4, 5].

The determination of pesticide residues in agricultural products, plant and environmental samples has been major subject for many years because of their potential risk on human health, persistence and tendency to bio-accumulate [6, 7].

The analysis of this class of compounds is carried out by means of several steps as: extraction from matrix, concentration of target compounds and finally instrumental separation and quantitatively determination. The quality of every process usually contributes to quality of the analytical results. During the extraction and enrichment step, the trace solutes are isolated from the matrix, and their
concentration is increased to enable their identification or quantification. In environmental and food safety fields, a large variety of extraction and enrichment techniques were reported [8, 9, 10].

The present method concerns the determination of target compounds: Lindane, Heptachlor, Aldrin, o,p-DDE, Dieldrin, Endrin, p,p'-DDT, and Methoxychlor in some food solid samples of commercial interest using Solid-Liquid Extraction procedures prior GC/MS analysis [11, 12, 13].

2. Materials and methods

2.1. Instruments

Analysis was performed on a Thermo Finnigan Trace GC interfaced with a Polaris Q ion trap mass spectrometer, operated in electron impact ionization (EI) mode. Electron energy was set at 70 eV and ion source at 230°C. Separations were carried out using a DB-5MS fused silica capillary column (30 m x 0.25 mm i.d., 0.5 µm film thickness). Helium was employed as the carrier gas with flow rate of 1.5 °ml/min at constant flow with vacuum compensation. One micro litres of a standard solution or sample extract were injected in the splitless mode at 250°C using the following program: 150°C, then 5°C/min ramp to 300°C. Total run time was 30 min.

2.2. Extraction

A quantity of 1 g of every sample of food supplement was weighed in a 10 ml centrifuge tube and then 5 ml of acetone was added. The tube was vigorously shaken for 3 min using a Vortex mixer and afterwards, centrifuged at 9.000 rpm for 5 min. The extracted samples were concentrated to dryness and then dissolved in isooctane. The final extract was adjusted to 0.5 ml in a dry flow of argon and then injected (2 µl of extract) in a GC/MS system. Diphenylamine was used as surrogate standard.

![Figure 1. Separation of pesticides using GC/MS system](image-url)
3. Results and Discussion

The main objective of this study was to develop a rapid method based on the solid-liquid extraction and GC/MS system for analysis of common pesticides in food samples at low mg/kg. The lindane, heptachlor, o,p-DDE, p,p’-DDT, aldrin, dieldrin, endrin, metoxychlor were chosen because their appear frequently in the food products [14, 15].

Figure 1 shows the separation of the selected groups of pesticides by GC/MS system.

The recoveries were determined by using a food sample spiked with different amounts of analytes and the calculated quantities compared with the spiked concentrations. Every point was obtained as a mean of three different determination of the same concentration. Recovery factors values are greater than 86%, except for heptachlor for which the recovery factor is of 75%.

The relation between compound concentration and chromatographic peak area in all shows a linear equation having correlation coefficient ($R^2$) better than 0.913 in the range from 0.04 µg/g to 4 µg/g.

The limit of quantification (LOQ) was obtained for every compounds corresponding at an amount of a signal three times greater than noise. The obtained values are under 0.040 µg/g.

The experimental values obtained for retention time ($t_R$), correlation coefficient ($R^2$), recovery factors ($R_f$) and limit of quantification (LOQ) are presented in Table 1.

| Compound   | $t_R$ (min.) | $R^2$     | $R_f$ (%) | LOQ µg/g |
|------------|--------------|-----------|-----------|----------|
| Lindane    | 12.56        | 0.9311    | 90.44     | 0.008    |
| Heptachlor | 15.39        | 0.9735    | 75.00     | 0.041    |
| Aldrin     | 16.80        | 0.9134    | 86.38     | 0.015    |
| o,p-DDE    | 19.90        | 0.9199    | 80.27     | 0.002    |
| Dieldrin   | 21.18        | 0.9451    | 98.63     | 0.012    |
| Endrin     | 22.10        | 0.9284    | 88.88     | 0.040    |
| p,p’-DDT   | 23.14        | 0.9291    | 86.44     | 0.016    |
| Metoxychlor| 27.20        | 0.9516    | 84.33     | 0.015    |

The results obtained for few samples of food supplement are shown in Table 2.

Three target compounds were determined above of LOQ in the samples of plant extract $S_1$ (raspberry), $S_2$ (maize), $S_3$ (cranberry), $S_4$ (rose) and $S_5$ (horsetail). The detected quantity was under 0.23 µg/g. The detected compounds are: Lindane, DDT and Metoxychlor.

| Compound     | $S_1$     | $S_2$     | $S_3$     | $S_4$     | $S_5$     |
|--------------|-----------|-----------|-----------|-----------|-----------|
| Lindane      | -         | 0.230±0.025| -         | -         | 0.076±0.009|
| Heptachlor   | -         | -         | -         | -         | -         |
| Aldrin       | -         | -         | -         | -         | -         |
| o,p-DDE      | -         | -         | -         | -         | -         |
| Dieldrin     | -         | -         | -         | -         | -         |
| Endrin       | -         | -         | -         | -         | -         |
| p,p’-DDT     | -         | 0.142±0.018| -         | 0.110±0.021| -         |
| Metoxychlor  | 0.031±0.002| 0.052±0.007| 0.080±0.013| 0.011±0.003| -         |

4. Conclusion

Using suitable solvent in a solid-liquid extraction procedure of pesticides, the food samples can be investigated in a reasonable time (around of few hours) by GC/MS. In every investigated food sample
was detected traces of chlorinated pesticides. The maximum concentration was for Lindane (0.23 µg/g in sample S2).

5. References

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