CHROMATOGRAPHIC METHODS FOR DETERMINATION OF HERBICIDE RESIDUES IN VARIOUS MATRICES

Irina COROI[1], **G. JITĂREANU**[1]

[1] University of Agricultural Sciences and Veterinary Medicine, Iaşi; *e-mail: coroirina@yahoo.com*

Modern agriculture depends to a large degree on the use of herbicides in order to cotrol weeds that compete with the crops. Herbicides are widely used in agricultural crops to control weeds they may produce important yield reductions. The introduction of these pesticides in the food chain via the environment can be considered a risk for human health due to the toxicity of the most of these compounds. In the last years, new extraction procedures have been developed to overcome the drawbacks caused by using high amounts of glassware and toxic solvents in the classical liquid extraction methods. The newest results in the use of various extraction techniques and chromatographic methods such as high-performance liquid chromatography and gas-chromatography mass spectrometry used for the assessment of herbicide residue in various matrices have been compiled an critically evaluated.The objectives of these review are the concise enumeration of the chromatographic separation methods used for the determination of herbicide residue in various organic and anorganic matrices, and the compilation and critical evaluation of the most meaningful results.

***Key words:** herbicide residues, extraction methods, GS-MS*

The contamination of soil, surface and ground water with pesticides from agriculture applications is a major problem. Herbicides represents about 50% of the demand for agricultural chemicals and are applied directly or indirectly to increase crop yields. Herbicides protect crops from undue competition from weeds and enhance the nutrion quality of food. Their prolonged use involves the risk of their retention and accumulation not only in soil and crops, but also in ground and agricultural waters, so the analysis of these compounds has become an important part of water and soil monitoring programmes.

The main chemical classes of herbicides include triazine derivates containing three heterocycle nitrogen atoms in the ring structure (atrazine, prometryn, metribuzyn etc.), clorophenoxy acid derivates (2,4 – D etc.), substituted chloroacetanilides (alachlor, propachlor etc.), urea derivates, substituted sulphonylureas (amidosulfuron, nicosulfuron, etc.).

Because of the wide variety of molecular structures of herbicides, the development of a considerable number of chromatographic separation methods was necessitated for their successful analysis.

Because of their excellent separation capacity, various chromatographic techniques have found acceptance and application for the separation and quantitative determination of herbicide residue in different organic and anorganic matrices.

The objectives of these review are the enumeration of the chromatographic separation methods used for the determination of herbicide residue in various organic and anorganic matrices, and the compilation and critical evaluation of the most meaningful results.

MATERIAL AND METHOD

As pollutants, herbicide are present in very low concentration and they have to be separated from the majority of the components of the accompanying matrix and enriched before analysis. The selection of the most effective extraction is very important for the reliable measurement of herbicides. Herbicides may be extracted directly from water, groundwater and wastewater or might need to be filtered prior the procedure.

Liquid liquid extraction has frecvently been used for ennrichment of selected sample constituient. The efficacy of the method is generally high but requiers highly purified and expensive solvents. Some solvents may endanger the health of laboratory staff and increase environmental pollution when discarded.

A considerable number of alternative extraction technique has been developed and applied in the measurement of herbicides residue.

Accelerated solvent extraction is an extraction tehnique that speeds the extraction process and reduces the total amount of solvent used. The system uses conventional solvent (ethyl acetate/cyclohexane or $MeCl_2$/acetone, 1:1, v/v) at elevated temperatures (100^oC) and pressures (10 MPa), which results in improved extraction kinetics. The extraction of the sample requires 1 to 30 g, 12 – 17 minutes and 15 – 50 mL of solvent. The samples were weighed and then are transfered to the extraction cells.

Solid – phase extraction uses a solid sorbent filled in a short column, where the herbicides residue are retained and selectively eluted with an appropriate solvent systems. The selection of the most effective sorbent, depends on the physicochemical charactere of the herbicide and the components of the accompanying matrix (Pico et all., 2000).

Some other extraction methods such as continuous – flow liquid membrane extraction (Chao et al., 2002), class – selective immunoextraction using various immunosorbents, pressurized liquid extraction and microwave – assisted extraction have also been found application.

The efficacy of each individual extraction have been documented.

Herbicide residue in various matrices (soil, water, cereals)

As a result of agricultural practices, the soils are polluted by herbicides, they enter mainly by spraying operation. After extraction and preconcentration technique the herbicide residues are analysed by chromatographyc methods. Herbicides such as trifluralin, simazine and two degradation products from environmental water sample, were extracted with ethyl acetate in a mechanical shaker for 50 min. Following the extraction, the supernatant was dried through anhydrous sodium sulphate, concentrated and analysed by high resolution gas chromatography with thermionic specific detection (Luciana Polese, et al., 2002). The average recoveries at different fortifications levels were > 70% with relative standard deviation < 19% and detection limits ranged from 0.023 to 0.088µgL^{-1}.

Soil samples were placed in a polypropylene column and extracted with 4 ml of ethyl acetate for 15 min in an ultrasonic water bath. After drying the soil samples were extracted again by sonication with another 4 ml of ethyl acetate (15 min) and then the samples was washed with additional solvent (2 ml). Two capillary columns, HP-1 (crosslinked dymethyl siloxane) and HP-1701 (cyanopropylphenyl methyl siloxane), 30 X 0.25 mm I.D. ,film thickness were compared . The oven temperature was kept at 80^{0}C for 1 min and then programmed at 5^{0}C min^{-1} to 250^{0}C, held 15 min. The average recoveries varied from 89% to 109% with a relative standard deviation between 2% and 10%, and the detection limit of the method ranged from 0.001 to 0.02 µg g^{-1} respectively. Because of its reproducibility and sensitivity, the method has been propesed for the analysis of alachlor, metribuzin, cyanazine, bromacil from soil samples.

Because of their importance in human nutrition has been developed an adequate analytical technique for the study of the effect of herbicides on quality of the agricultural products and quantitative determination of herbicides in crops. Herbicides present in soil and water can pollute crops and can enter in food chain. Fruit and vegetables can be directly polluted by herbicides or they can be polluted by taking up herbicides from contaminated soil or surface and groundwater. Gas chromatography mainly with MS detection has been employed for the determination of herbicide residue (acetochlor, propanil, atrazine and metribuzin) in soybean crop. The samples are extracted with acetone water (2:1) and purified through solid phase extraction with Florisil with an eluant of *n*-hexane-ether (15mL) at a flow rate of 0.5 mL/min. The eluant collected was dried with a nitrogen gas drier, and the remainder was dissolved with 1.0 mL *n*-hexane, which was ready for GC analysis. Separation was performed on a DB-1701, 30m X 0.25 mm i.d. x 0.25 µm, and carrier gas was nitrogen. The injector temperature was 270^{0}C and the initial temperature was 70^{0}C (for 1 min) and then raised to 200^{0}C at a speed of 15^{0}C/min (for 1 min). the average recoveries of soybean samples range from 63.3% to 96.0%, and the relative standard deviations are from 2.14% to 11.2%. Cereals contain a lot of lipids, proteins and phospholipids, which makes the pre- processing hard, results in low recovery, and brings serious interference to chromatographic analysis however are time and effort consuming and employ a lot of poisonous reagents**.**

CONCLUSIONS

A large variety of methods have been used in the determination of herbicides in soil, preconcentration and prepurification are decisive steps in the determination of this class of pollutants.

The efficacy of the extraction determines the reliability of the subsequent chromatographic separation and quantification.

The development of sorbents with higher adsorption capacity and enhanced selectivity is needed to increase the performance of the whole analytical system.

The majority of extraction steps have been time- consuming and now the proposed procedure are simple and economic, require only small volumes of solvent and then decreasing the hazard for both human health and the environmental.

BIBLIOGRAPHY

1. Dores, Eliana, F.G.C., Sandro Navickiene, 2006 - *Multiresidue determination of herbicides in environmental waters from Primavera do Leste Region (middle west of Brasil) by SPE-GS-NPD.* J. Braz. Chem. Soc. Vol. 17 no.5 Sao Paulo.
2. Polese, Luciana, 2002 - *Determination of herbicides residue in soil by small scale extraction*. Eclet. Quim. Vol.27 Sao Paulo.
3. Libing, Wang, Cao, Li, 2008 - *A rapid multi-residue determination mehod of herbicides in grain by GS-MS-SIM. Journal of Chromatographic Science,* Vol. 46, p. 424-429.
4. Chao, J., Liu J., 200 - *Determination of sulfonylurea herbicides by continuous flow liquid membrane extraction on line coupled with high – performance liquid chromatography*. Journal of Chromatography; 955: 183 – 189.
5. Pico, Y., Font G., 2000 - *Solid phase extraction of quaternary ammonium herbicides.* Journal of Chromatography; 987: 375 – 380.