A Review of Liquid Chromatography in Environmental Pesticide Analysis*

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Liquid chromatography
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Summary
The use of liquid chromatography in environmental pesticide analysis is reviewed. In addition to classical UV and electrochemical detectors, detection systems such as mass spectrometry and gas chromatography-type detectors are discussed. The applicability of supercritical fluid chromatography to pesticide analysis is also reviewed.

Introduction
Currently pesticides used on a worldwide scale include organophosphorus and carbamate pesticides, triazine, phenylurea or chlorophenoxy acid herbicides. Since many of the organochlorine pesticides have been withdrawn from use because of evidence on their toxicity, persistence and bioaccumulation in the environment, the organophosphorus compounds have become an important group replacing the organochlorine pesticides in many agricultural applications.

Organophosphorus pesticides show persistence in soil for a maximum of 3 months, which is the lowest value for all the different groups of pesticides, (about 8 month for phenoxy herbicides, 12 months for carbamates and more than 16 months for urea triazine herbicides [1]). Capillary gas chromatography (GC) with thermionic (TID) [2] or flame photometric detection (FPD) [3] and capillary GC-mass spectrometry (MS) in the electron capture, electrical conductivity or MS detection [24–26]. However, the problem of the thermal instability of such compounds can be solved by using LC, with either UV [15, 28–30], electrochemical [31] or MS detection avoiding thermal decomposition of methyl ureas to isocyanates or amines [32–34].

Analytical methods presently used for the separation of triazine herbicides include gas chromatography [35–39] but advantages claimed for the LC method are its suitability for higher molecular weight herbicides, polar herbicides or metabolites, and thermally labile compounds [40–45]. The phenoxyalkyl acid herbicides are examples of selective growth stimulating herbicides and have been used since the forties to control many types of broadleaved, herbaceous, and woody weeds in cereals, lawns and pasture lands [46]. The analysis of such polar compounds with low vapour pressure is in general simpler by means of LC [47–49], since for GC, volatile derivatives have to be used [46].

Analytical procedures for the determination of carbamate pesticides are rather limited too. This group of pesticides is thermally labile which prevents direct analysis by GC but, LC is ideally suited for carbamate separation either employing electrochemical detectors [50], a precolumn clean-up step with fluorescence detection [51] or MS [32, 49, 52].

In this review, the development of different LC systems for pesticide environmental analysis is reviewed, either using conventional LC detectors, such as UV or electro-
Precolumn Technology

A well-known approach in sample preparation procedures is to enrich trace components of interest on solid sorbents in order to isolate and preconcentrate them prior to their separation and detection. Sorbents such as carbon, alumina, silica, alkylsilane-modified silica or porous polymers contained in a plastic cartridge or short stainless steel or glass column, are called solid-phase extraction columns, or precolumns, when operated on-line with a chromatographic separation column. The general functions of the solid-phase extraction columns are trace enrichment, clean-up, storage of samples, protection of the main column and derivatization, as has been clearly described by Frei et al. [53]

Different applications have been developed for the analysis of different groups of herbicides such as phenylureas and triazines, mainly in water samples, using UV, electrochemical or MS detection. A typical automatic pre-concentration apparatus has been described elsewhere [28]. This LC system from Kontron (Zürich, Switzerland) consisted of two model 410 pumps, a model 200 programmer, an MCS 670 column-switching apparatus and a Uvikon LC 720 variable wavelength UV detector set at 241 nm. Separations were usually carried out using a reversed phase C-18 column and pre-columns packed with RP-8, RP-18 and 2-amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) support. Such a pre-concentration system has been applied to the residue analysis of phenylurea herbicides and their corresponding anilines in water. It should be pointed out that in the determination of phenylureas a special problem is the discrimination between these analytes and the substituted anilines which are their main (bio) degradation products. Discrimination between a single herbicide and its corresponding aniline can easily be achieved by means of LC. A special platinum phase packed in a short pre-column acted as an aniline filter for a group separation of the herbicides from anilines. The coupling of such a Pt pre-column with a C-18 pre-column permits pre-concentration of the herbicides, on-line transfer and separation on a reversed-phase analytical column. The feasibility of the method was demonstrated by analyzing river water samples spiked with seven herbicides and seven anilines. The application of ACDA-Pt allows the removal of at least 0.1 ppm of anilines from aqueous solutions containing 5–10 ppb phenylurea herbicides, so that automatic sample clean-up and pre-concentration of river water samples can be achieved by reversed-phase LC with UV detection. A similar approach has been applied by the same group [31] using electrochemical detection to phenylurea herbicides using on-line trace enrichment on a small C-18 pre-column followed by analysis on a C-18 column. Sensitivities reached the order of sub-ppb in surface water samples. Selective determinations (at 1.0 V) of Metuxoron in the presence of other phenylureas allowed the detection of 30 ppt of herbicides in surface water.

Liquid chromatography with on-line preconcentration has been used for the determination at ppb level of the fungicide Iprodione (1-isopropylcarbamoyl-3-(3',5'-dichlorophenyl) hydantoin) [54] in surface water. Detection was by UV at 229 nm and the resulting chromatograms were free of interferences. Detection limits were 0.02 ppb with good reproducibility and easy automation. A similar system has been also applied to the determination of residues of N-methylcarbamate pesticides, such as Propoxur, Carbofuran and Carbaryl, in extracts of total diet [51]. In such cases the automated clean-up procedure using pre-column switching gave excellent results by using at the same time post-column derivatization with o-phthalaldeyde (OPA) and fluorescence detection. The limits of detection were at the low ppb level (0.3) with extremely difficult matrices, such as total diet homogenates. Analysis of Bromacil, Diuron and 3,4-dichloroaniline in contaminated well water [29] was achieved using basically the column switching procedure described earlier. The method used reversed-phase LC with UV detection at 254 nm and direct sampling of water containing 1.3 μg/l and 0.048 μg/l of Bromacil and Diuron, respectively, onto the post-column. Hamman and Kettrup [47] have developed a method for trace analysis of phenoxyl acid herbicides in water samples at the low ppb level by employing on-line enrichment with detection at 280 and 230 nm.

Precolumn technology has also been applied to phenylurea herbicides using a mass spectrometer detector [33]. Aqueous solutions containing six phenylurea herbicides were loaded onto the precolumn at a flow rate of 500 μl/min. Acetonitrile:water (70:30) at 200 μl/min was used for both desorption and LC separation. Before the LC mobile phase entered into the MS a split of 90:10 was done, so only 10% of the mobile phase was directed into the MS source. It has been shown that, with relatively non-polar compounds, on-line trace enrichment can give a considerable improvement in sensitivity (from 200 ppm to 10 ppb) with little additional band broadening.

Coupling of sample handling techniques with selective detectors provides a powerful analytical system. In addition, such a system can be fully automated to handle samples as complex as total-diet homogenate or polluted water sources and they can be tailor-made to solve specific problems. They can be easily applied to different groups of herbicides employing available detectors.

Post-Column Reaction and Extraction Detectors

The weakest part of an LC system is still the detector because of the limited possibilities of UV/VIS and fluorescence detectors. It is only possible to detect components