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Large volume sample stacking in capillary zone electrophoresis for the monitoring of the degradation products of metribuzin in environmental samples

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Abstract

A capillary zone electrophoresis (CZE) method with UV–vis detection has been developed for the simultaneous monitoring of the major degradation products of metribuzin, i.e. deaminometribuzin (DA), deaminodiketometribuzin (DADK) and diketometribuzin (DK). The dissociation acid constants have also been estimated by CE and no significant differences have been observed with the values obtained by applying other techniques. Optimum separation has been achieved in less than 9 min in 40 mM sodium tetraborate buffer, pH 9.5 by applying a voltage of 15 kV at 25 °C and using *p*-aminobenzoic acid as internal standard. In order to increase sensitivity, large volume sample stacking (LVSS) with polarity switching has been applied as on-line pre-concentration methodology. Detection limits of 10, 10 and 20 ng/mL for DA, DADK and DK, respectively were obtained. The method has been applied to soil samples, after pressurized liquid extraction (PLE). Samples were extracted at high temperature (103 °C and 1500 psi) using methanol as extraction solvent and sodium sulphate as drying agent. This PLE procedure was followed by an off-line pre-concentration and sample clean-up procedure by solid-phase extraction (SPE) using a LiChrolut EN sorbent column. These last two procedures were also suitable for the direct treatment of groundwater samples before CE analysis. The combination of both off-line and on-line pre-concentration procedures provided a significant improvement in sensitivity. LVSS provided pre-concentration factors of 4, 36 and 28 for DK, DA and DADK, respectively and with SPE a pre-concentration of 500-fold for the case of water samples and of 2.5-fold in the case of soil samples was obtained. The method is suitable for the monitoring of these residues in environmental samples with high sensitivity, precision and satisfactory recoveries.
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Keywords: Acid dissociation constants; Capillary zone electrophoresis; Metribuzin degradation products; Pressurized liquid extraction; Environmental samples; Large volume sample stacking

1. Introduction

The use of herbicides is connected with a risk of pollution of the subsoil and consequently with contamination of groundwater and domestic water resources. Thus, the leaching of herbicides has been intensively studied during the last years in order to characterise the pollution and attenuation potential. Until now, extensive research has been conducted regarding the occurrence of herbicides in the environment; however, current understanding of the biological impacts of herbicide use is limited by the fact that most investigations have been focused on the active ingredients (parent compounds) without considering their transformation products (depredates). For an understanding of the fate of herbicides in soil and water, the inclusion of metabolites is crucial because they can be present at higher levels in the environment than the parent pesticide itself [1–3].

Metribuzin is a selective systemic herbicide used for pre- and post-emergence control of many grasses and broad-leaved weeds in soy beans, potatoes, tomatoes, sugar cane, alfalfa, asparagus, maize and cereals at 0.07–1.05 kg a.i./ha [4]. Metribuzin belongs to the group of triazinone herbicides, it is highly water-soluble (1.05 g/L) and adsorption in low-organic sandy soils

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is rather weak, sorption coefficients vary from 0.56 in a very sandy loam to 31.7 in a soil containing 60% organic matter [5]. Metribuzin is considered to be of short to moderate persistence in soils, the half-lives measured have been specified between 5 and 50 days. The decomposition of metribuzin in the environment is due to microbiological and chemical processes. The primary products from metribuzin transformation in soil are deaminometribuzin (DA), diketometribuzin (DK) and deaminodiketometribuzin (DADK). Metribuzin degradation happens through microbiological and chemical processes, generating diketometribuzin (DK), deaminometribuzin (DA) and deaminodiketometribuzin (DADK) like degradation majority products, and two conjugated glycosides like minority products. The microbiological and photolytic processes of degradation give rise to the deamination and the desulphuration of the original active principle. The total degradation of metribuzin, until transforming into water and carbon dioxide, happens through DADK. Other unidentified metabolites are detected in experiments using ^{14}C-labeled metribuzin. Total degradation of metribuzin to inorganic species (mineralization) is usually below 10% of the metribuzin applied; thus, stable and persistent metabolites may be accumulated in the soil [6]. Fig. 1 shows the generally accepted degradation pathway of metribuzin.

Usually the analysis of metribuzin and its degradation products has been accomplished by different chromatographic methods such as reversed-phase thin-layer chromatography (RP-TLC) with UV detection [7] or high-performance liquid chromatography (HPLC) with diode array detection [8,9] or mass spectrometry detection [5,10,11]. Capillary electrophoresis (CE) presents a very interesting alternative to chromatographic method for the analysis of pesticide residues and by-products in environmental samples, due to its low cost, short separation times, high efficiency and no need of high volumes of organic solvents. Although CE has been used to separate metribuzin from others pesticides in multi-residue determinations using micellar electrokinetic chromatography (MEKC) [12,13] or CE in presence of cyclodextrin using laser-induced fluorescence [14], but only recently a MEKC procedure, based on the use of sodium dodecyl sulphate (SDS), has been developed for determining simultaneously metribuzin and its degradation products in soil samples [15], considering the neutral nature of metribuzin which prevents its determination by capillary zone electrophoresis (CZE). In this case, detection limits of 23, 22 and 20 $\mu g\,kg^{-1}$ were obtained from DA, DK and DADK. However, the anionic properties of the degradation products of metribuzin could allow the determination by CZE, which can be easily combined with several on-column sample pre-concentration methods to increase the amount of the analyte introduced into the capillary in order to obtain an improvement in sensitivity. Some reviews have been published about different on-line sample stacking techniques in CE [16–22]. Among the different modes, the simplest one is normal stacking mode (NSM), which is done by dissolving the sample in a low conductivity matrix and by injecting the resulting sample solution hydrodynamically. Focusing happens at the interface between the low conductivity matrix and the buffer due to the abrupt change in electrophoretic velocity. A limitation of NSM is the short optimum sample plug length that can be injected into the capillary without loss of separation efficiency or resolution [17]. However, large volume sample stacking (LVSS) [23] implies the introduction of a volume greater that found optimum in NSM. In this case, the sample matrix must be pumped out from the capillary in order to preserve separation efficiency. Pumping is carried out with external pressure or with EOF, the direction of pumping always being opposite that of the electrophoretic movement of charged solutes and its velocity lower than the electrophoretic velocity of the charged solutes. Using this strategy, only positive or negative solutes can be effectively concentrated at one time. Concentration factors of more than 100 are reported for LVSS, improving the limit of detection (LOD) by two orders of magnitude. In LVSS two modalities exists, with or without change of polarity. For the case of anions, LVSS with polarity switching is a mode that permits to control the electroosmotic flow (EOF) in CZE separations involving high EOF conditions to carry the separate analytes to the detector. This is done by introducing hydrodynamically a large plug of low conductivity sample into the capillary and applying negative voltage at the injection end. The large solvent plug is then electroosmotically pushed out the capillary while the negative species stack-up at the boundary between the sample zone and the background electrolyte. Once the main part of the low conductivity zone has been pushed out of the capillary, the positive voltage is applied to carry out the separation.

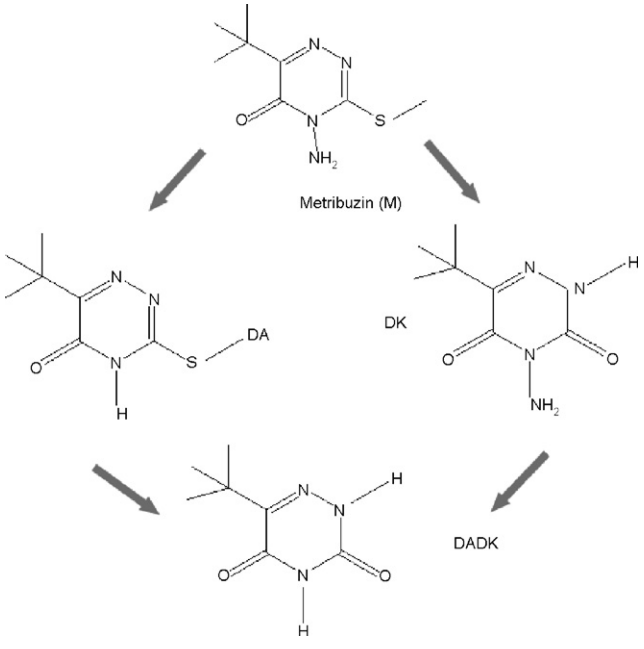

Fig. 1. Likely degradation pathways of metribuzin. DA: Deaminometribuzin; DK: diketometribuzin; DADK: deaminodiketometribuzin.

Ionization constants of herbicides and their metabolites in general have been shown to be important in studies of soil adsorption and aqueous solubility. Ionic binding to soil constituents, which decreases effective herbicidal activity, has been postulated to be related in a predictable manner to the pK_a values of the herbicides. In addition, ionization constants and their relation to lipophilicity are important parameters to the study

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