

15th Danube-Kris-Mures-Tisza (DKMT) Euroregion Conference on Environment and Health

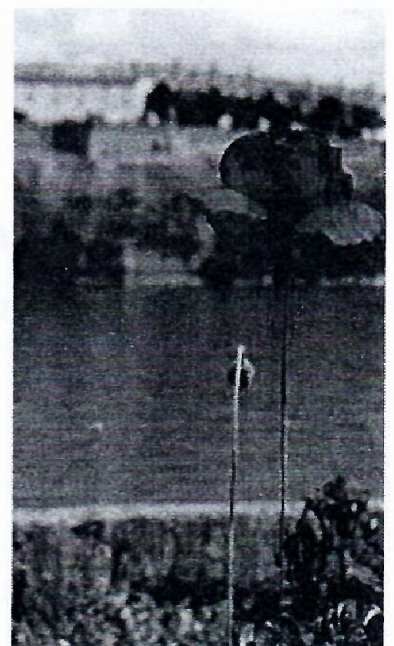


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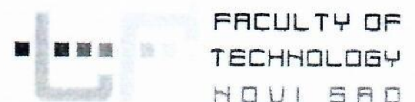
LACREMED Conference

“Sustainable agricultural production:
restoration of agricultural soil quality by remediation”

PROCEEDINGS



University of Novi Sad
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by remediation“

University of Novi Sad, Faculty of Technology,
Novi Sad, Serbia, 16-17 May 2013

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SOLID-PHASE EXTRACTION OF DICAMBA HERBICIDE FROM WATER

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Abstract

The purpose of this study was to examine the extraction of dicamba residues in water by two types of SPE cartridge - Strata X-AW and Oasis HLB. Residues were determined using a HPLC/DAD. The results showed that the both extraction approaches are a good method for determination of dicamba in water.

Key words: dicamba; residue; SP extraction; water

Introduction

Human population is constantly exposed to numerous chemical species present in the environment. Among these compounds, chlorophenoxy acid herbicides are of significant importance because of their wide distribution and extensive use as plant growth regulators.

Chlorinated acids are selective agricultural herbicides which are widely employed in agriculture and gardening for control the growth of different unwanted vegetable species in crops. Because of high water solubility and toxicological risk of some acid herbicides and their metabolic products, monitoring of their concentration in surface and groundwater is very important task. The acidic herbicides are manufactured in formulation as free acids, as their alkaline salts or as esters. The unionized free acids vary in water solubility, but the acidic herbicides most frequently exist in ionized form at environmental pH values. Acidic herbicides formulated as salts are water soluble, while those formulations prepared as esters are less water soluble. In the environment, acidic herbicides formulated as esters have short hydrolysis half-life time (24–48 h) and therefore they are generally present as ionized acids.

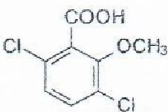
Dicamba (3,6-dichloro-2-methoxybenzoic acid) is a benzoic acid derivative herbicide used for the control of annual and perennial broadleaf weeds in grain crops and grasslands. In combination with a phenoxyalkanoic acid or other herbicide, dicamba is used in pastures, range land, and non-crop areas such as fence-rows and roadways to control weeds. When applied, they are easily transferred to surface and ground waters due to their polar nature and good solubility. Dicamba is highly soluble in water and as an acid with a pKa of 1.95 (Table 1), it is highly mobile in the soil (Herbicide Handbook, 1983; Johnson and Sims, 1998) and may contaminate water supplies (Smith and Bridges, 1996; Cole et al., 1997). As a result, dicamba has been detected in groundwater, farm ponds, and streams (Grover et al., 1997; Frank et al., 1990a; Frank et al., 1990b). The results of the prior studies show that dicamba may persist for several weeks after spray in soil depending on the weather and soil condition (Moyer et al., 1992; Burnside and Lavy, 1966; Friesen, 1965; Serim and Maden, 2012).

Herbicide residue analysis generally requires several steps, such as extraction of the pesticide from the sample of interest, removal of interfering co-extractives and identification and quantification of the pesticide content (Das, 1981).

For most analytes, especially for the acidic herbicides, solid phase extraction (SPE) is the choice of sample treatment, which is followed by appropriate chromatographic separation and sensitive determination of target components. For the acidic herbicides, combination of physico-chemical parameters influences their extraction from aqueous solution. Ionogenicity

(pK_a) and hydrophobicity ($\log K_{ow}$) (Hansch et al., 1995) are especially important in determining the approach of SPE for efficient sample clean-up for further chromatographic analysis of chlorophenoxy acid herbicide in water samples.

Table 1. Physico-chemical properties of dicamba acidic herbicide

Common name/ molecular formula/ CAS No.	Systematic name	Structure	pK_a	Aqueous solubility (mg/l)	$\log K_{ow}$
Dicamba $C_8H_6Cl_2O_3$ (1918-00-9)	3,6-dichloro-2- methoxy- benzoic acid		1.95	4500	2.21

The acidic herbicides are polar and non-volatile compounds, and do not lend themselves to direct analysis by gas chromatography. Using high performance liquid chromatography (HPLC) the acidic herbicides can be analyzed in the ionic form, the molecular unionized acid form or as the ester.

The purpose of this study was to examine the extraction of dicamba residues in water by two types of SPE cartridge. Residues were determined using a liquid chromatograph equipped with a diode array detector (HPLC/DAD).

Materials and methods

Materials

Dicamba analytical standard was provided by Dr Ehrenstorfer (Augsburg, Germany). Solvents for standard solutions, extraction and mobile phase were obtained from different suppliers: acetonitrile, methanol and diethyl ether (MTBE) from JT Baker (Netherlands), as well as formic acid; ammonium hydroxide from Zorka, Šabac. Deionised water was prepared through the water system (TKA, Germany). For solid-phase extraction (SPE) two types of cartridges were used - Strata X-AW by Phenomenex and Oasis HLB provided by Waters.

Analytical procedures

Method validation was performed by analysing freshly spiked tap water samples with appropriate amount of dicamba acid herbicide. SPE analysis was performed using Strata X-AW and Oasis HLB cartridges.

Extraction

StrataTM X- AW (60 mg/3 ml) is a polymer- based weak anion exchange sorbent. The active functional group is a diamino ligand containing both primary and secondary amines. Prior to extraction cartridges was conditioned with 2 ml of mixture methanol/formic acid (98/2, v/v), followed by 5 ml of deionized water. Afterward, 50 ml of fortified tap water was transferred to the SPE cartridge reservoir and eluted through the cartridges. For the cartridge washing 2 ml of deionized water and 2 ml of methanol were used. After drying 1-3 min, the analyte was eluted with 2 ml of MeOH/NH₄OH (98/2, v/v). The elution solvent was evaporated to dryness at 30 °C.

The extract was dissolved in 1 ml of mixture methanol/water, ultrasonically homogenized and analyzed by HPLC/DAD.

Oasis HLB Cartridge (60 mg/3 ml). Before the sample was loaded the cartridge was conditioned with 3 ml of mixture methanol/MTBE (10/90, v/v), 3 ml of methanol and 2 ml of water. Then, under vacuum 50 ml of spiked water sample was filtered through the cartridge. Afterward, cartridge was washed with 1 ml of water. Dicamba eluted with 2 ml of mixture methanol/MTBE (10/90, v/v), evaporated to dryness, reconstituted in 1 ml of mixture methanol/water and analyzed by HPLC/DAD.

HPLC-DAD analysis

Analysis was performed by using a liquid chromatograph (Agilent 1100 Series, USA), equipped with a diode array detector (DAD). The HPLC system was controlled by ChemStation software. The separation was achieved on Zorbax C₁₈ (50 mm × 4.6 mm, 1.8 μm) at 25 °C. The mobile phase used was 13 mM phosphate buffer pH 3.4 and acetonitrile. Dicamba was determined at wavelength of 210 nm by use of a DAD. The injection volume was 10 μl.

Results and discussion

The optimum mobile phase consisting of the 13 mM phosphate buffer pH 3.4 (A) and acetonitrile (B) (80:20, v/v) and elution with linear gradient was finally used for determination. Dicamba absorbance was in the UV spectrum range, with maximum around 210 nm. The 25°C column temperature was chosen as an optimum. At the flow rate 1.0 ml/min the analyte dicamba was sufficiently separated. Besides the regularly shaped and well-defined peaks belonging to the investigated dicamba pesticide, the SPE-HPLC-DAD chromatograms (Figure 1) contained of peaks which probably have origin from the solvent/mobile phase. There were no significant interfering peaks in the elution region of dicamba pesticide.

The correlation coefficient (R^2) for the linear regression curve was found more than 0.993 in the range of 0.1-10 μg/ml. The retention time of dicamba was 1.327 minute. The repeatability of the retention times and peak areas were checked by injecting the standard dicamba solution five times. The relative standard deviations (*RSD*) of the retention times and peak areas were found to be less than 0.5%.

For the recovery studies 50 ml of tap water spiked with dicamba acid herbicide in concentration levels of 0.5, 2 and 5 μg/ml. Fortified samples extracted at previously described procedures. Average recovery obtained with Strata X-AW cartridges varied from 85.2 to 94.3% with the associated relative standard deviations (*RSDs*) ranging from 1 to 4%. Method accuracy achieved with HLB Oasis cartridges ranged between 86.9-95.8% (*RSDs* 2-5%).

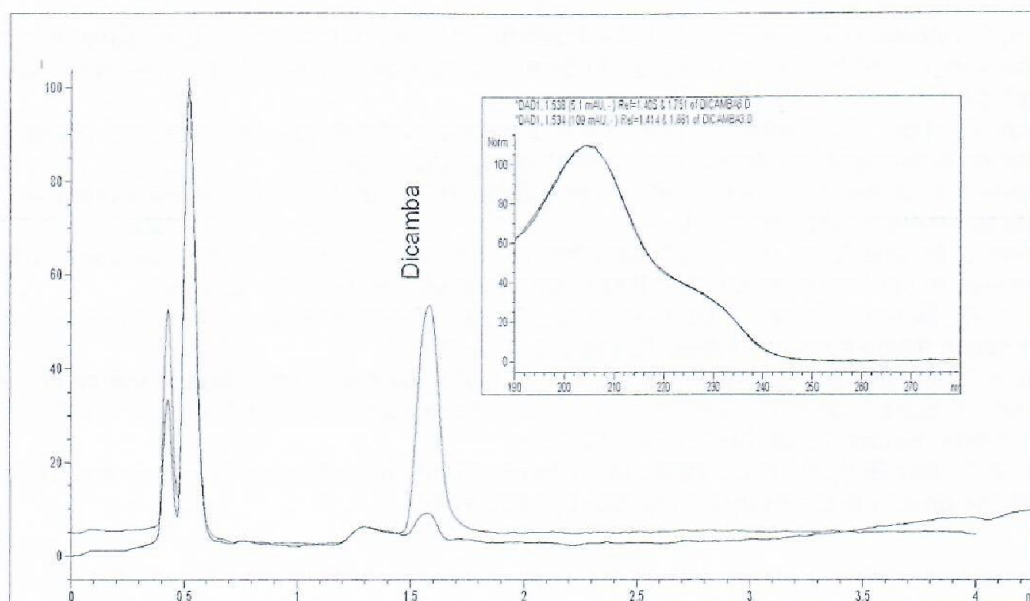


Figure 1. Comparison of chromatograms and the appropriate UV apex spectrums (as insets) of dicamba herbicide peaks of fortified tap water extract (lower) and standard dicamba solution (upper)

Conclusion

A method for determination of dicamba residues in water using two types of SPE cartridges and HPLC/DAD has been described. From the above results it was concluded that the both extraction approaches are a good method for determination of acidic herbicide, such as dicamba, in water samples. When comparing the results, it was evident that the Strata X-AW and Oasis HLB cartridges gave the high values of the recovery. Considering the EU MRL for individual pesticide in water for human consumption (European Commission, 1998), the results show that the extraction and analysis procedures are efficient for determination of dicamba in water.

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