BEHAVIOR OF HERBICIDE BENSULFURON-METHYL IN MICROWAVE-ASSISTED SOLVENT EXTRACTION (MASE) FROM SOILS WITH DIFFERENT PHYSICOCHEMICAL CHARACTERISTICS

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ABSTRACT

The feasibility of MASE application in the determination of Bensulfuron-methyl (BSM) in soils with different organic matter content, consequently with a different capability to adsorb this herbicide is studied. Hydrolysis experiments were performed to check the significance of degradation under various temperature and time conditions in aqueous-acetonitrile solutions at various pH. Results are shown of the application of the method developed in the determination of BSM in two characteristic Chilean soils (organic matter content 1.4 and 11.4 % and pH 7.2 and 5.1, respectively). The maximum temperature that can be used during the heating program is 60°C, where the two main degradation products were undetected and recovery percentages reached 95%.

Key Words: Bensulfuron-methyl; Microwave Assisted Solvent Extraction, MASE, soil samples

INTRODUCTION

Bensulfuron-methyl (BSM, methyl 2 –[(4,6-dimethoxypyrimidin-2-yl) carbamoyl sulfamoyl methyl] benzoate) is a systemic sulfonylurea herbicide used at a low dose. Its main chemical degradation reaction is the cleavage of the sulfonylurea bridge, yielding methyl 2 (amino sulfonyl methyl) benzoate and 4,6-dimethoxy-2-aminopyrimidine, the reaction rate being highly pH sensitive (1, 2). Methods for the determination of sulfonylureas in soil and water samples include mainly high performance liquid chromatography (HPLC) with UV, MS and photoconductivity detection (3-7). Extraction with an alkaline aqueous solvent or a mixture of alkaline aqueous/organic solvent followed by cleanup using either solid-phase extraction or liquid-liquid extraction is a common approach for the determination of sulfonylureas herbicides in soil. These procedures are time consuming and co-extracted soluble humic substances usually generate severe degree of interferences in the determination at low concentration levels with HPLC. Microwave-assisted solvent extraction (MASE) has been successfully applied for the extraction of cinosulfuron, thifensulfuron-methyl, metsulfuron-methyl, sulfometuron-methyl and chlorsulfuron in soil samples (8). The overall objective of this study was to investigate the feasibility of MASE application in the determination of BSM in soils with different organic matter content, consequently with a different capability to adsorb this herbicide. Taking into account that BSM hydrolysis rate increases with a decreasing pH and becomes more important at higher temperatures, the behavior of this compound at different extraction conditions was studied. HPLC with photodiode array detection (HPLC-DAD) was selected for instrumental analysis. DAD allowed determining both the stability of the organic compound and the interferences from co-extracted compounds from soils.

Reagents and standard solutions.

BSM (Chem Service) and the degradation products, 2 (amino sulfonyl methyl) benzoate and 4,6-dimethoxy-2-aminopyrimidine (Dupont), purity > 99 % were used. Acetonitrile was HPLC grade (J.T. Baker) and water was purified with a NANO pure™ analytical deionization system (Barnstead, Thermolyne Corporation). NaOH and HCl were analytical grade (Merck).

Equipment

A HPLC chromatograph Waters equipped with a quaternary gradient pump (Model 600), an autosampler (Model 717 Plus), a PDA detector (Model 996) and the Millenium 2010 Software was used. PDA instrumental parameters were: wavelength, 200-300 nm; acquisition rate, 1 spectra/second; spectral resolution, 1.2 nm. The separation column was a Zorbax SB-C_8, 80 Å, 4.6 x 150mm, 5 mm particle size with a Zorbax XDB C_{18} 4 x 4 mm, guard cartridge.

Extractions were performed with a Milestone MLS-1200 Mega microwave digestion system configured with a MDR-1000/6 carousel. A temperature control system (ATC-300) allowed the automatic monitoring and control of preset temperature values inside a reference vessel during a sample digestion procedure.

Chromatographic Analysis

The starting mobile phase composition was H_2O (pH 2.8, adjusted with H_3PO_4) - CH_3CN in the ratio 70:30 (flow rate 1.5 ml min^{-1}). CH_3CN was linearly increased for 1 min to reach 55%, which was maintained for 4 min to return to the initial condition in 1 min and finally hold for 6 min. BSM was quantified at 235.2 nm, and its retention time was 6.5 min (column temperature 35°C). The retention times for 2 (amino sulfonyl methyl) benzoate and 4,6-dimethoxy-2-aminopyrimidine were 2.7 and 2.2 min, respectively. Degradation products were detected but not quantified.

Soil Samples

One non-allophanic soil from the V Region of Chile (Pocuro, PCR) and one allophanic soil from the IX Region (Temuco, TEM) were used

to verify the applicability of the extraction technique. The most relevant physicochemical properties are the following: organic matter (OM) content 1.4% and 11.4% and pH 7.2 and 5.1 for PCR and TEM soils, respectively.

K_f values from the empirical Freundlich relationship describing adsorption behavior of BSM were 2.4 and 19.8 cm^3/g.

Hydrolysis Experiments

Hydrolysis behavior as a function of pH and temperature was studied taking into account classic experimental conditions to be employed in the extraction of the organic compound from soils by using microwaves energy. Aqueous solutions at a concentration level of 5.2 µg/ml were prepared at pH 3.1, 4.8, 6.9 and 9.4 (pH was controlled with diluted solutions of HCl and NaOH). 1 ml of each solution and 5 ml of acetonitrile were mixed, and incubated at 4 different temperatures in a water bath: 25, 50, 75, and 90°C. Incubations were carried out for 5 and 10 minutes; finally, the corresponding tubes were cooled down inside an ice bath for 10 min.

MASE Procedure

Freshly spiked soil samples were obtained by weighing 1.00 g of each soil into the extraction vessels followed by the addition of 1 ml of aqueous spiking solution at 4.0 µg ml^{-1}; the samples were equilibrated by shaking for 1 h before extraction. Subsequently, 5 mL of acetonitrile were added to each vessel. The use of aged spiked samples in this preliminary study was discarded due to the degradation behavior of BSM in soils. The adsorption of BSM has been described as a very fast process, the equilibrium being reached in the first 30 min in different kinds of soils (9). All samples were extracted in duplicate and 6 simultaneous extractions were always performed. Blank tests for soils were carried out to evaluate co-extracted components. The starting parameter settings in the microwave system were: 2 min at 350 W, 3 min at 500 W and, finally, a 2 min vent step at 0 W. Once the digestion program was completed the rotor was cooled down for 15 min before opening the vessels. The extraction system was studied at 60, 70, and 80°C in the second step. In all cases the first step was performed at 40°C. An additional run was developed without temperature control. Monitoring of temperature values inside the vessel during the whole digestion procedure was always performed. After the extraction, vessel contents were centrifuged at 4000 rpm for 15 min and filtered through a 0.22 mm membrane (GV, Durapore) into a vial for chromatographic analysis.

Limit of detection (LOD) and limit of quantification (LOQ) for the chromatographic determination of BSM were calculated from the data set obtained from a linear calibration curve (0.02, 0.05, 0.10, 0.15 and 0.20 µg ml^{-1}, two replicates for each standard) according with the following equation (10):

$$LOD = 3\left(S_{Y/X}/b\right)\sqrt{\frac{n-2}{n-1}}$$

Where b and $S_{Y/X}$ are the slope and the regression standard deviation values, respectively. LOQ was determined by multiplying by 10 in this equation. The corresponding values were 8 x 10^{-3} and 2.7 x 10^{-2} µg ml^{-1}. The chromatographic response within this range was linear with an r^2 value of 0.9983.

The aim of the previous hydrolysis experiments was to check the significance of degradation under different conditions likely to be present inside the vessels during an extraction run. The effect of moisture content of soil samples on the recoveries of different kinds of organic compounds by MASE has been described (11,12), so this is one of the parameters frequently optimized. Consequently, the addition of water to a dried sample soil to normalize the moisture content will generate different conditions of pH, as a function of soil properties that could affect the degradation behavior of the herbicide during the extraction process. On the other hand, the application of microwave energy could give a non-controlled increase of the temperature. Results from the experiments taking into account these parameters are shown in Table 1. Good recoveries with values higher than 95% were obtained at 25 and 50°C with no chromatographic evidence of degradation. At 75° C, values were significantly lower at all pH and particularly for the more extended times. At the intermediate pH, usually existing in the soil solution, at the lower incubation time, degradation was scarce or less significant at this temperature. This trend was also observed at the highest temperature; nevertheless, disappearance was far too intensive to consider this condition as a choice for an appropriate extraction of BSM from soils.

Table 1. Mean recovery of Bensulfuron-methyl in aqueous-acetonitrile solutions at various pH and temperatures.

	25°C		50°C		75°C		90°C	
Time (min)	5	10	5	10	5	10	5	10
pH								
3.1	97,3	97,2	97,2	95,9	84,7	71,6	52,7	38,2
4.8	100,0	99,7	97,5	96,6	94,3	76,8	76,1	35,5
6.9	99,0	98,5	96,4	95,7	94,8	81,5	66,3	34,3
9.4	98,5	97,2	98,1	96,6	91,9	90,5	47,1	42,2

Increased reactivity with decreasing pH has been reported for this herbicide. Hydrolysis rate constant obtained at pH 4 and 40°C is 25 and 4.5 times greater than those of pH 7 and 10 at the same temperature, respectively (2). Temperature effects for the acid-catalyzed hydrolysis has also been stated, the rate constant at 40°C being 18 greater than that obtained at 22°C. Figure 1 shows chromatograms obtained in the incubation experiments during 10 min at 25°C and 90°C. Appropriate values for spectrum matching and purity testing in these runs were obtained, giving a spectrally homogeneous peak for BSM and its hydrolysis products (when degradation was observed), the only exception being for the pyrimidine amine at pH 3.1, where an spectroscopic evidence for a co-eluted compound was established. In this experimental condition a more complex degradation pattern was observed.

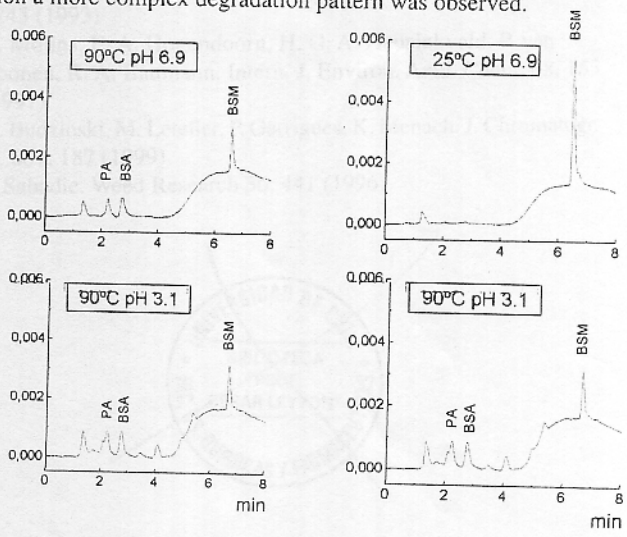

Fig. 1. Chromatograms obtained for the incubation at various pH and temperatures. BSM=Bensulfuron-methyl, PA=pyrimidine amine;

BSA=benzylsulfonamide. The cleavage of the sulfonylurea bridge followed by a secondary cyclization of the benzyl sulfonamide to [1H-2, 3-benzothiazin-4.(3H)-one 2,2-dioxide] has been described (1). The pyrimidine ring cleavage has also been observed under acidic pH. At pH 9.4 and 90°C a greater dissipation without any significant detection of the degradation products was observed, probably due to a consecutive decomposition of them at the temperature under study. Transformation of the benzyl sulfonamide by cyclization is very pH sensitive, i.e., almost immediate above pH 10 (13).

Mean recoveries of BSM through the MASE procedure above described were: 94.9, 90.5, 73.5 and 3.5 % for the extractions carried out at 60, 70 and 80°C and without temperature control respectively for PCR soil, and 94.3, 88.4, 66.1 and 1%, for TEM soil, at the same conditions. Monitoring showed that maximum temperatures reached during the different heating programs were 64, 72, 83, and 120°C, the latter corresponding to the program without temperature control. Figure 2 shows two chromatograms obtained for PCR soil for the extractions performed at 80 and 120°C. Almost a total degradation of the herbicide is produced when no control is used, the parent and the two principal hydrolysis compounds being detected at a trace level. The pyrimidine amine and the benzyl sulfonamide were undetected after extractions developed at 60 and 70°C. At 80°C both compounds were observed, but peak purity of the first one demonstrated the co-elution of some soil constituent co-extracted through the analytical procedure, blank test showing the same impurity at the same retention time.

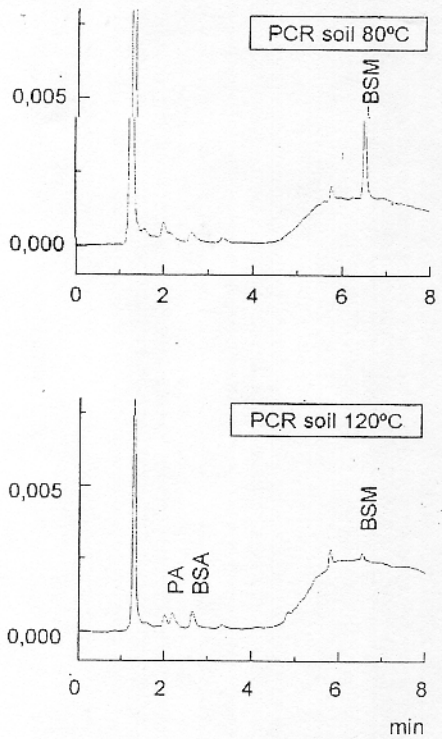

Fig. 2. Chromatograms of extracts of PCR soil obtained by MASE developed at 80°C and 120°C.

The results for the extraction method agree with the analysis done above. The slightly lower recoveries obtained for TEM soil can be explained mainly by its high capability to adsorb BSM, possibly as a result of the high organic matter content, and not through a greater degradation originated in the heating program or in an acidic-catalyzed hydrolysis. In addition, these results indicate that some differences may be found on the analyte recovery, related to the type of soil, illustrating the need to optimize conditions, specially for soils with a high organic matter content.

From these preliminary results we can conclude that the application of MASE in the extraction of BSM from soils is feasible. However, accurate temperature control and optimization of the different parameters of the heating programs or several sample related parameters have to be done. Efforts will be directed to obtain the better analytical conditions to reach appropriate LOD and LOQ to the determination of BSM at the low concentrations to be expected in sample soils as a function of the low concentrations used to achieve an efficient herbicide activity.

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