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ASSESSMENT OF SIX HERBICIDES FROM VARIOUS CLASSES IN PLANTS BODY PARTS BY A NOVEL GC-MS/MS METHOD

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Introduction

The need to increase agricultural production has led to the use of herbicides in pest control. In Europe and the USA, herbicides represent 44% of the total pesticides used in 2012. Three important classes of herbicides are diphenylether herbicides (e.g oxyfluorfen, acifluorfen, aclonifen, bifenox), pyrimidine herbicides (e.g diquat dibromide, paraquat, lenacil, chloridazone, foramsulfuron) and carbamic herbicides (e.g chlorprofam, prosulfocarb, triallate). In this study a GC-MS/MS method for evaluation of six herbicides from these classes was developed for their evaluation in vegetal matrices. As sunflower is one of the crops that use large quantities of these herbicides, stem and leafs of young sunflower plants were used as vegetal matrix. Excepting Chlorprofam, banned in EU in 2019, product containing studied herbicides are available for sale on farming shops. According to European legislation, the concentration of herbicides cannot exceed 0.01 mg/Kg in vegetal material.

Materials and methods

All substances used were purchased as analytical purity standards from Sigma Aldrich (Oxyfluorfen and Triallat) and Dr. Ehrenstorfer (Prosulfocarb, Bifenox, Aclonifen and Chlorpropham).

Sun flower plants selected as vegetal matrix were taken from the area adjacent to Bucharest, Romania. The sample was taken in May 2022 and the stem was sectioned at ground level. After sampling, the plants were cleaned of insects, sectioned and divided into leaves and stem. Some of the leaves were shredded and turned into a paste. The whole leaves (A), the shredded leaves (B) and the stems (C) were dried at 80 ° C for 24 hours. The extraction of sunflower tissues resulted in intense green or brown-brown extracts that could not be analyzed directly by GC-MS / MS. Purification of plant extracts was performed by passing through the column loaded with silica gel and anhydrous sodium sulfate, using hexane for elution.

For MS screening, monitoring was performed in the range of 50-500 uam in EI mode.

For identification and quantification of compounds GC-MS / MS Thermo TSQ 8000 Evo - gas chromatograph, GC 1310, coupled with mass spectrometer with triple quadrupoles arranged in tandem. GC-MS conditions: capillary column 5% phenyl, 95% dimethylpolysiloxane, 60 m long, 0.25 mm inside diameter and 0.25 μm stationary phase thickness injection mode: split (10:1), injector temperature: 280°C,

carrier gas (He) flow rate: 1.2 mL / min, Oven temperature: 50°C for 2 minutes; heating with 20˚C / min up to 200°C, then with 20°C / min up to 280°C; maintaining the temperature at 300°C for 11 minutes, transfer line temperature: 300°C, ionization chamber temperature: 250°C, positive EI mode, 70 eV, volume: 1 µL, SRM transitions used: Chlorpropham: 213 → 127 (C), 213 →171 (Q); Triallat: 268 → 86 (C), 268 → 128 (Q); Prosulfocarb: 251 → 128 (C), 251 → 91 (Q); Oxyfluorfen: 361 → 252 (C), 361 → 300 (Q); Aclonifen: 264 → 212 (C), 264 → 194 (Q); Bifenox: 341 → 310 (C), 341 → 189 (Q).

Results and conclusions

MS screening of organic extracts showed no synthetic compounds used as herbicides or insecticides. Most identified compounds consisted in natural terpenoids. None of the selected herbicides were identified in vegetal samples collected.

Table 1. Recovery of herbicides in vegetal matrix

Compound	Sample mg/Kg	Expected value mg/Kg	A mg/Kg	B mg/Kg	C mg/Kg
Prosulfocarb	<0.005	0.047	0.0277	0.0281	0.0275
Bifenox	<0.005	0.051	0.0365	0.0365	0.0344
Chlorpropham	<0.005	0.048	0.0327	0.0320	0.0315
Aclonifen	<0.005	0.049	0.0245	0.0245	0.0292
Oxyfluorfen	<0.005	0.048	0.0306	0.0296	0.0308
Triallat	<0.005	0.048	0.0359	0.0337	0.0354

The calibration ranges for the studied compounds described good linearity from 10 to 500 µg/L, corresponding to 0.005-0.25 mg/Kg in samples. For method evaluation, enriched samples were used and recovery yield varied between 59% (Prosulfocarb) and 73% (Triallate), Table 1.

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