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FAST AND SENSITIVE GC-MS/MS METHOD FOR DETECTION OF SOME AUXIN HERBICIDES RESIDUES IN ENVIRONMENTAL SAMPLES

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Introduction

GC-MS/MS method are often used in analytical determination of pesticides due to its high sensitivity, compounds selectivity and good separation. Auxin pyridine herbicides as clopyralid, dicamba, triclopyr and fluroxypyr are polar compounds which require structural modifications in order to be volatilized and then separated on most used capillary columns. Because there are limited applications of *in-port* derivatizations and GC-MS/MS detections of these herbicides, a new method for these compounds was developed. Silylation reactions, especially with MTBSTFA, are mainly chose as an alternative to alkylation in order to avoid secondary interference products.

The above mentioned compounds are usually found in environmental samples, like surface water, soil and biota.

Materials and methods

The indicated analytes from 100 mL water sample acidified to pH 2 were extracted using Dionex AutoTrace 280 SPE on Strata-X (1000 mg) cartridges (Thermo Scientific SPE HyperSep). The adsorbed compounds were eluted with 10 mL ethyl acetate. The extracts were concentrated to1 mL, dried with anhydrous magnesium sulphate and derivatized with 10 µL MTBSTFA (1% t-BDMCS).

The analysis was completed by a Thermo Trace 1310 gas chromatograph coupled with a triple quadrupole mass spectrometer (MS/MS) TSQ 8000 Evo. The GC is equipped with a PTV (programmed temperature vaporizing) injector. The PTV used settings are: 1 µL extract is injected at 150°C in splitless mode, evaporated in 1 min at 200°C with 14°C/sec rate. At the same rate the compounds were injected in a 1 ml/min He (6.0 purity) flow rate and separated on a TG-5SILMS column (60 m, 0.25 mm x 0.25 µm). The MS/MS conditions were: 300 ºC transfer line, 250ºC for analytes ionization (70 eV, EI) and 5-40 eV collision energies applied for ion fragmentation in second quadrupole. In this method was used as internal standard pentachloronitrobenzene, added before the extraction step.

Results and conclusions

In this work, four herbicides were succesfully quantified on a GC-MS/MS method. In order to achieve the optimum results, were varied some operational conditions parameters, which are specific for:

- programmed temperature vaporizer injector (PTVi): injection temperature, evaporation temperature and time, transfer rate temperature, MTBSTFA volume;
- MS/MS detection: selecting the SRM transitions (single reaction monitoring), collision energy.

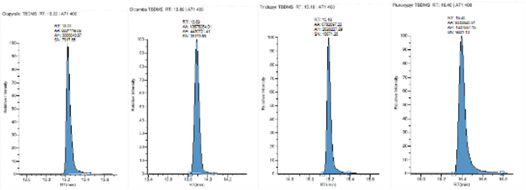

Figure 1. Graphic representation of selected analytes peaks

The obtained results show a good linear regression in the range of 1-100 (200) µg/L with a determination coefficient (R^2) higher than 0.9930. By choosing the optimum two SRMs for each compounds, the developed method is sensitive enough to determine the instrumental quantification limit below 0.17 µg/L.

The GC-MS/MS method was applied to the determination of auxin herbicides from 100 mL water samples, after a solid phase extraction (SPE) step on polystyrene/polydivinylbenzene copolymer adsorbant. Because the derivatisation reaction took place directly into the PTV inlet (*in situ*), the reaction time and preparation samples steps were reduced.

Table 1. Performance parameters

	t_R (min)	**Instrumental calibration range (µg/L)**	**IQL (µg/L)**	**R^2**	**LOD (µg/L)**	**LOQ (µg/L)**
Clopiralid	13.23	1-100	0.17	0.9996	0.003	0.010
Dicamba	13.90	1-100	0.025	0.9934	0.003	0.011
Triclopir	15.19	1-200	0.035	0.9971	0.002	0.008
Fluroxipir	16.39	1-200	0.020	0.9971	0.003	0.010

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