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GC-MS/MS METHOD FOR TRACE ANALYSIS OF CHLOROPHENOXY ACIDIC HERBICIDES FROM WATER SAMPLES

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Introduction

A sensitive GC-MS/MS method was developed for the determination of five important chlorophenoxyacetic herbicides from surface water: 2,4 D (2,4-dichlorophenoxyacetic acid), MCPA (4-chloro-2-methylphenoxyacetic acid), 2,4 DB (2,4-dichlorophenoxybutyric acid), MCPB (4-chloro-2-methylphenoxybutyric acid), 4 CPA (4-chlorophenoxyacetic acid). The analytical challenge in the determination of the acidic herbicides by GC consists in an additional derivatization step due to the -COOH polar group. GC-MS/MS is used to increase the sensitivity for the quantification of TBDMS (*t*-butyldimethylsilyl) derivatives which are often used in MS separations because of the easily fragmentation of molecular ion.

Materials and methods

A volume of 200 mL distilled water sample spiked with 100 µg/L herbicide mix and acidified to pH 2 with H₃PO₄ 85% was extracted on Thermo Scientific SPE HyperSep C18 (1000 mg) cartridges at 10 mL/min using an automated solid phase extraction Dionex AutoTrace 280 SPE. The adsorbed compounds were eluted with 6 mL ethyl acetate at a 5 mL/min rate. The extract was concentrated to 1 mL, then dried with anhydrous sodium sulphate to eliminate any moisture for the proper derivatization with 10 µL MTBSTFA (with 1% *t*-BDMCS). Before injection it was added syringe internal standard (PCB 209) to 100 µg/L final concentration. The analytes were determined with a Thermo Trace GC 1310 coupled with a tandem mass spectrometer (MS/MS) TSQ 8000 Evo. A volume of 2 µL extract was injected in constant split less mode at 260°C. The compounds were separated with 1 mL/min He flow on a TG-5MT column (60 m, 0.25 mm x 0.25 µm) using an oven temperature program starting from 50 °C (1 min) to 230 °C (25 °C, 1 min) then to 290 °C (8 °C/min, 9.5 min). The compounds are ionised through electronic impact (70eV, 250 °C). The full scan was performed at 50-450 m/z. In order to obtain the highest intensities for optimum ion transitions (SRM – single reaction monitoring) it was applied 5 or 10 eV collision energy.

Results and conclusions

The main results concerning SPE optimization show that C18 cartridges extraction is more efficient, with 4-47% for all analytes, than on copolymer adsorbents Strata X

(polystyrene/polydivinylbenzene). By removing cartridge water conditioning step (10 mL, pH 2) the recovery results increased with 2.1-25.7%.

The applied method was validated by assessing the specific performance criteria as specificity, sensitivity (detection and quantification limits), linearity, precision and accuracy.

Limits of quantification of the method were decreased by choosing the highest intensities transition corresponding to the most abundant ions. The main fragments removed are *t*-butyl, methyl and CO. No other peaks were observed for the selected SRM.

Table 1. MS/MS working parameters

TBDMS Compound	[M] ⁺	SRM transitions	Collision energy eV	Quantification ion (Q) / Confirmation ion (C)
4 CPA	300.0	215 -> 197	10 eV	Q
		243 -> 215	5 eV	C
MCPA	314.6	257 -> 229	5 eV	Q
		257 -> 211	10 eV	C
2,4 D	335.0	277 -> 213	10 eV	Q
		277-> 249	5 eV	C
MCPB	342.7	285 -> 199	10 eV	Q
		285 -> 243	5 eV	C
2,4 DB	362.0	219 -> 183	10 eV	Q
		305 -> 219	10 eV	C

It was found that the regression is linear between 2-200 µg/L and 5-200 µg/L, with a determination coefficient (R²) higher than 0.9950. The quantification limit (LOQ) is lower than 3.3 ng/L for 200 mL water. The precision expressed as the relative standard deviation is the extraction repeatability of 6 replicates at 100 µg/L. The method recovery is acceptable, with values in the domain of 68.5-114%.

Table 2. Performance parameters

	t _R (min)	Instrumental calibration range (µg/L)	R ²	LOD (ng/L)	LOQ (ng/L)	Precision (RSD%)	Recovery (%)
4 CPA	12.84	5-200	0.9963	0.59	2.0	18.8	93.1
MCPA	13.45	5-200	0.9966	0.93	3.1	16.4	68.5
2,4 D	14.07	5-200	0.9980	0.99	3.3	9.6	73.7
MCPB	15.50	2-200	0.9976	0.51	1.7	5.2	114
2,4 DB	16.13	2-200	0.9967	0.59	2.0	7.5	87.9

The analyses of chlorophenoxy acids as TBDMS derivatives was validated through a SPE-GC-MS/MS method. SRM transitions are specific for the selected compounds. Concentrations of 2,4 D between 2.0-247 ng/L were found in wastewater samples by applying this method.

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