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Short Communication

Intra-injector formation of methyl esters from phenoxy acid pesticides

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ABSTRACT

Trimethylanilinium hydroxide was used as a derivatization agent for a broad range of phenoxy acids. Derivatization took place inside the injector immediately before gas chromatographic analysis, thereby minimizing the chance of exposing the operator to trimethylanilinium hydroxide. The reproducibility and sensitivity of the derivatization procedure were high. Maximum sensitivity for 19 phenoxy acids was 0.1–0.3 ppm. Derivatization was quantitative and did not produce by-products. The procedure required a minimum of time and effort compared with other derivatization methods in current use and is recommended for routine determinations of phenoxy acids.

INTRODUCTION

Phenoxy acids are widely used in forestry and agriculture as regulators of plant growth [1]. As an example, herbicides represent 80% of the crop protection chemicals used in Sweden, and phenoxy acids account for 65% of these herbicides [2]. An important characteristic of phenoxy acids is their selectivity. Phenoxy acids affect most of the dicotyledonous plants, whereas monocotyledonous plants and cereals are not influenced by the concentrations used in agriculture. Unfortunately, phenoxy acids are not sufficiently stable or volatile to be determined by gas chromatography (GC) without derivatization.

Several methods have been used for the derivatization of such acids. Cochrane [3] reviewed esterification and transesterification of phenoxy acids: 2,4-dichlorophenoxypropionic acid (2,4-D), 2,4,5-trichlorophenoxypropionic acid (2,4,5-T) and 4-chloro-2-methylphenoxyacetic acid (MCPA) have been esterified with sulphuric acid–*n*-propanol and 2,4-D and 2,4,5-T with sulphuric acid–methanol. Solutions of boron trifluoride in methanol, *n*-butanol or 2-chloroethanol have been applied to esterify 2,4-D, picloram, 2,4,5-T and other herbicidal acids. Further, diazomethane has been used to esterify 2,4-D, dicamba, MCPA, picloram and 2,4,5-T. Overall, diazomethane is the most frequently used derivatization agent for phenoxy acids but, because of the toxicity, carcinogenicity and explosiveness of

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this substance, alternative compounds are being sought.

In a previous study [4], we introduced trimethylanilinium hydroxide (TMAH) as a derivatization agent in the clinical laboratory for free fatty acids extracted from bateria. The aim of this study was to examine whether TMAH can be used for the derivatization of a broad range of phenoxy acids, and to see if this derivatization procedure can be carried safely out inside the injector. Phenoxy acids, which are derivatives from formic, acetic, propionic and butyric acids, undergo the same chemical reactions as do fatty acids [4–6].

EXPERIMENTAL

Chemicals

The phenoxy acid standards included in this study, their sources and their retention times (t_R) in the gas chromatograph used are given in Table I. MethElute methylating agent (Pierce Europe, Oud Beijerland, Netherlands), containing 0.2 *M* TMAH in anhydrous methanol, was also applied.

Sample preparation

Standards of phenoxy acids were dissolved in anhydrous methanol at concentrations of 1–2 ppm. Of this solution 100 μl were transferred using a Hamilton syringe to a glass vial and dried with nitrogen. The vial was closed and 100 μl of TMAH in methanol (see *Chemicals*) were injected into the vial after perforation of its closing rubber membrane. GC and GC–mass spectrometry (GC–MS) were performed immediately after derivatization and after storage of the derivatized phenoxy acids for 4 days.

GC of derivatized phenoxy acids

A Model 8700 gas chromatograph (Perkin-Elmer, Norwalk, CT, USA) was used with a fused-silica capillary column (15 m × 0.25 mm I.D.) with a film thickness of 0.25 μm of the stationary phase CP-Sil 5 methylphenylsilicone (Chrompack, Middelburg, Netherlands). Helium served as the carrier gas at a flow-rate of 2.0 ml/min. The temperature of the injector was 240°C and that of the flame ionization detector was 275°C. The column temperature programme was 90°C, held for 1 min, and then increased from 90 to 290°C at 6°C/min. The attenuator was set at 8. The chart paper speed was 10 mm/min. The sample (2 μl) was delivered as a splitless injection.

GC–MS

The instrument used for GC–MS consisted of a Model 8700 gas chromatograph furnished with an ion-trap detector (Perkin-Elmer). For the chromatographic conditions, see the previous section.

The derivatization procedure was controlled using 1 ppm of MCPA and MCPA methyl ester (Pestanal; Riedel-de Häen, Seelze, Germany). The reaction products were determined by GC–MS.

RESULTS AND DISCUSSION

The retention time of the TMAH reagent was less than 10 min (Fig. 1). Thereafter, the derivatized

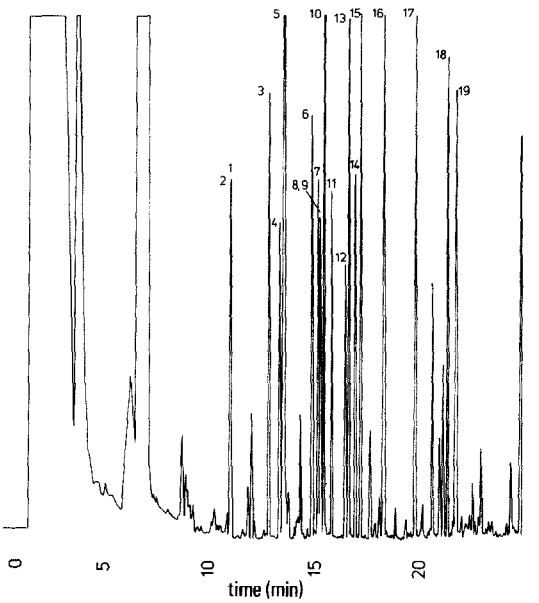

Fig. 1. Gas chromatogram of TMAH derivatized phenoxy acid standards. For conditions, see text. Peaks: 1 = 2-phenoxypropionic acid; 2 = *p*-fluorophenoxyacetic acid; 3 = 2-methylphenoxyacetic acid; 4 = 3-methylphenoxyacetic acid; 5 = 4-methylphenoxyacetic acid; 6 = 2-formylphenoxyacetic acid; 7 = 2,5-dimethylphenoxyacetic acid; 8 = 2-(4-chlorophenoxy)propionic acid; 9 = 2,4-dimethylphenoxyacetic acid; 10 = 2-methoxyphenoxyacetic acid; 11 = 4-phenoxybutyric acid; 12 = 3-methoxyphenoxyacetic acid; 13 = 4-methoxyphenoxyacetic acid, 14 = 2-(4-chloro-2-methylphenoxy)propionic acid; 15 = 4-chloro-2-methylphenoxyacetic acid; 16 = 2,4-dichlorophenoxypropionic acid; 17 = 4-iodophenoxyacetic acid; 18 = α-(2,4,5-trichlorophenoxy)propionic acid; 19 = 2,4,5-trichlorophenoxyacetic acid.

phenoxy acid standards appeared at various intervals (Table I, Fig. 1). The reproducibility of the TMAH derivatization procedure was high, as was its sensitivity. Based on five parallel measurements with a 1 ppm solution of MCPA (see under *GC–MS*), the S.D. was 3%. The maximum sensitivity for the nineteen phenoxy acids shown in Fig. 1 was 0.1–0.3 ppm. When only those phenoxy acids most frequently used in agriculture were considered, the sensitivity was 0.1–0.2 ppm. There was no difference in the chromatographic pattern of the immediately injected reaction mixture and the pattern of that injected after 4 days.

GC–MS fragmentation of the methyl ester from MCPA is shown in Fig. 2. The GC–MS fragmentation pattern agreed with that of the authentic standard. Derivatization with TMAH was quantitative and did not produce any by-products. Similar results were achieved with free fatty acids [4,6].

In order to test the methylphenylsilicone stationary phase, 300 injections were made into the column. No broadening of peaks or changes in retention values were observed. The chance of exposing the operator to TMAH was minimal as the derivatization occurred inside the injector immediately before GC.

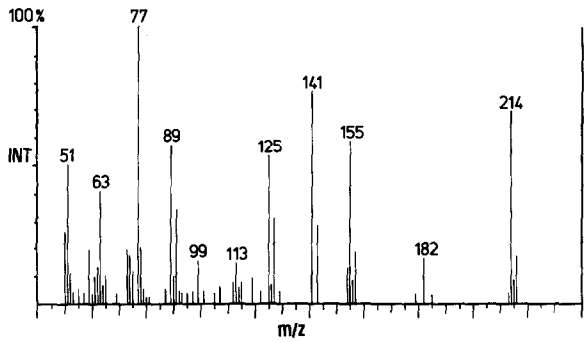

Fig. 2. Electron impact mass spectrum of the methyl ester from MCPA.

We have suggested "intra-injector derivatization" as a more appropriate term for this mode of

TABLE I

SOURCES AND RETENTION TIMES OF PHENOXY ACID STANDARDS EXAMINED BY GAS CHROMATOGRAPHY

Acid	Source	Retention time (min)
2-Phenoxypropionic	Janssen[a]	11.11
p-Fluorophenoxyacetic	Janssen	11.16
2-Methylphenoxyacetic	Ventron[b]	13.00
3-Methylphenoxyacetic	Ventron	13.45
4-Methylphenoxyacetic	Ventron	13.60
2-Formylphenoxyacetic	Ventron	14.85
2,5-Dimethylphenoxyacetic	Ventron	15.00
2-(4-Chlorophenoxy)propionic	Janssen	15.25
2,4-Dimethylphenoxyacetic	Ventron	15.30
2-Methoxyphenoxyacetic	Ventron	15.60
4-Phenoxybutyric	Ventron	15.90
3-Methoxyphenoxyacetic	Ventron	16.70
4-Methoxyphenoxyacetic	Ventron	16.85
2-(4-Chloro-2-methylphenoxy)propionic	Aldrich-Chemie[c]	17.05
4-Chloro-2-methylphenoxyacetic	Aldrich-Chemie	17.30
2,4-Dichlorophenoxypropionic	Sigma[d]	18.30
4-Idophenoxyacetic	Ventron	19.90
α-(2,4,5-Trichlorophenoxy)propionic	Sigma	21.40
2,4,5-Trichlorophenoxyacetic	Aldrich-Chemie	21.80

[a] Janssen Chemica, Beerse, Belgium.
[b] Ventron, Karlsruhe, Germany.
[c] Aldrich-Chemie, Steinheim, Germany.
[d] Sigma, St. Louis, MO, USA.

derivatization than "on-column derivatization" [4]. TMAH in methanol has, according to our information, not previously been used for the derivatization of a broad range of phenoxy acids. The procedure requires a minimum of time and effort compared with other derivatization methods in current use [3] and is recommended for routine determinations of phenoxy acids.

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