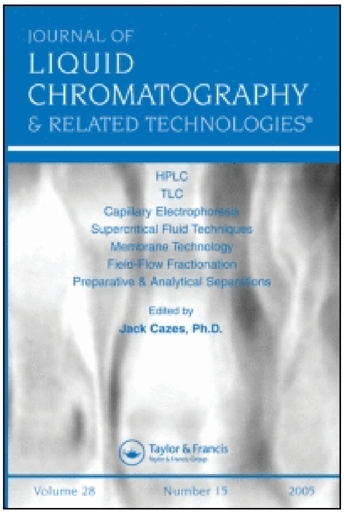

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HPLC METHOD FOR THE DETERMINATION OF CARBAMIC HERBICIDES IN FORMULATED PRODUCTS

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ABSTRACT

A summary of five papers for the analysis of karbutilate, chlorpropham, phenmedipham, triallate and sulfallate, by reversed-phase HPLC, with internal and external standard, in formulated products, is given.

Actually the methods for the above five mentioned herbicides are considered the same, the use of external or internal standard being the only remarkable difference.

A suggestion is made about the possibility of using this method for the analysis of all the carbamic herbicides.

INTRODUCTION

Carbamic herbicides form a useful and wide family of pesticides with the only common property of being related to the carbamic acid, but presenting great differences among themselves not only from the biological but from the physico-chemical point of view.

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Several methods have been proposed for the analysis of their formulations (1-5) according to the distinct chemical nature of every herbicide; nevertheless we thought that a general procedure could be developed with the aid of HPLC. To verify our thinking and not to have to work with all the members of this family, five of the most chemically different carbamic herbicides were chosen: N-alkyl-carbamates (karbutilate), N-aryl-carbamates (chlorpropham), bis-carbamates (phenmedipham), thiocarbamates (triallate) and dithiocarbamates (sulfallate). The first one as wettable powder (WP) and the others as emulsifiable concentrates (EC).

Two high-performance liquid chromatographic procedures, External and Internal standard methods, for the five above mentioned pesticides, have been published independently (6-10). This paper summarizes all of them.

EXPERIMENTAL

Apparatus

High-performance liquid chromatograph Hewlett-Packard 1084B equipped with microprocessor, RP-8 chromatographic column, and Millipore filters as described in a previous paper (8).

Reagents and chromatographic conditions

Solvents for preparing the different dilutions in the case of EC or extraction when analyzing WP, eluents for HPLC, internal standards, concentrations of external and internal standard solutions, and chromatographic conditions are shown in Table I. Injection volume, column temperature, and attenuation, were always the same: 10 µL, 40 ºC and 2^8, respectively.

RESULTS AND DISCUSSION

The number of analyses for every sample as well as the number of injections (chromatographic runs) for every analysis, in order to maintain a precision lower than 1% ($P = 0.01$), the optimum working space, the retention time, and the concentration of active ingredient with s and s_r, in the different formulated products, by the External standard method, are given in Table II. The same data, by the Internal standard method, as well as the molar absorptivities at the wavelengths of measurement, are summarized in Table III.

The highest point of every optimum working space is at least 30 times greater than the respective lowest one, so in all cases there is a wide space

Table I. Reagents and chromatographic conditions.

	KARBUTILATE	CHLORPROPHAM	PHENMEDIPHAM	TRIALLATE	SULFALLATE
Solvent	CH_3OH	CH_3OH/H_2O (65/35)	CH_3OH	CH_3OH/H_2O (90/10)	CH_3OH
Eluent	CH_3CN/H_2O (45/55)	CH_3OH/H_2O (60/40)	CH_3CN/H_2O (45/55)	CH_3CN/H_2O (60/40)	CH_3CN/H_2O (48/52)
Internal standard	linuron	4-nitro-di-phenyl-ether	4-nitro-di-phenyl-ether	di-n-pentyl-phtalate	linuron
External standard conc.*	0.12	0.20	0.10	0.40	0.32
Internal standard conc.*	0.20	0.90	0.68	0.80	0.15
Flow (mL min^{-1})	1.2	2.0	1.8	1.8	2.2
Wavelength (nm)	240	240	240	220	254
Detection limit (ng)	1.2	3.9	2.5	7.8	6.1

* mg mL^{-1}

Table II. Results (External standard method)

	KARBUTILATE	CHLORPROPHAM	PHENMEDIPHAM	TRIALLATE	SULFALLATE
No. of analyses	4	1	3	1	2
No. of injections	1	3	3	2	1
OWS (µg)	0.281-9.006	0.122-15.557	0.079-10.150	0.488-15.604	0.768-24.568
RT (min)	4.23	4.35	5.07	7.44	8.73
Concentration of a.i.	78.0 ± 0.74	41.9 ± 0.13	15.5 ± 0.10	39.2 ± 0.18	46.6 ± 0.33
s	0.71	0.13	0.09	0.15	0.31
s_r	0.90	0.30	0.55	0.38	0.67

OWS = optimum working space; RT = retention time; a.i.= active ingredient; s = standard deviation; s_r = relative standard deviation.

Table III. Results (Internal standard method) and molar absorptivity

	KARBUTILATE	CHLORPROPHAM	PHENMEDIPHAM	TRIALLATE	SULFALLATE
No. of analyses	4	1	1	2	1
No. of injections	1	1	3	1	1
OWS (µg)	0.293-9.381	0.117-14.984	0.381-6.100	0.488-31.245	0.777-24.869
RT (min) (herb-IS)	4.28-8.10	4.39-5.90	5.18-10.58	7.63-9.62	8.73-4.17
Concentration of a. i.	79.5 ± 0.82	41.3 ± 0.08	15.9 ± 0.10	39.2 ± 0.17	47.4 ± 0.17
s	0.78	0.08	0.05	0.16	0.16
s_r	0.98	0.19	0.34	0.40	0.35
Molar absorptivity x 10^{-4}	1.98	1.66	3.48	1.30	0.78

OWS = optimum working space; RT = retention time; (herb-IS) = herbicide-internal standard; a.i. = active ingredient; s = standard deviation; s_r = relative standard deviation.

of working. For phenmedipham and triallate this space is twice greater by the Internal than by the External standard method.

Chromatographic runs are always shorter than 12 min and notably inferior in many cases, specially by the External standard method, except for sulfallate where the internal standard appears before the corresponding herbicide.

The number of analyses and/or injections can be reduced by using an internal standard with all the herbicides, except karbutilate where those numbers are the same in both methods.

Precision is better by the Internal standard method for phenmedipham and sulfallate, and the same by both methods for karbutilate, chlorpropham, and triallate, s_r being always smaller than 1.

Statistically, there is not any difference between the means, at P = 0.01, by both methods, except sulfallate where it is significative, probably due to the great precision reached.

The data supplied by this paper, in relation to five of the most different carbamic herbicides, supported by the work of Sparacino and Hines (11) about the separation of some 30 pure carbamic pesticides, suggest that it is possible to use the proposed HPLC method for the analysis of every carbamic herbicide, only with small modifications according to the physico-chemical properties of each compound.

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