Gas chromatographic determination of acephate in technical products and in the formulations

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A method is presented for the determination of acephate (*O*,*S*-dimethyl *N*-acetylphosphoroamidothioate) in the presence of its technologically and toxicologically most relevant impurities: *O*,*O*-dimethyl phosphoroamidothioate, *O*,*O*-dimethyl *N*-acetylphosphoroamidothioate, *O*,*S*-dimethyl phosphoroamidothioate (methamidophos).

Besides, the conditions and parameters for g.l.c. analysis of *O*,*O*-dimethyl *N*-acetylphosphoroamidothioate, the technological precursor of acephate, are given.

Приводится метод определения ацефата (*O*,*S*-диметил-*N*-ацетиламидотиофосфата) в присутствии технологически и токсикологически самых существенных загрязнений: *O*,*O*-диметиламидотиофосфата, *O*,*O*-диметил-*N*-ацетиламидотиофосфата и *O*,*S*-диметиламидотиофосфата (метамидофоса).

Одновременно описывается отдельное определение *O*,*O*-диметил-*N*-ацетиламидотиофосфата как технологического промежуточного продукта.

Acephate is the active ingredient of insecticide formulations known under the commercial name of Orthene®. The biological properties and use of acephate in pest control are well known [1]. However, less is known about the g.l.c. analysis of acephate. The only method describing the analysis of technical and formulated acephate is the g.l.c. method of Carlstrom [2], which does not include the analysis of impurities. Besides, methods exist for the determination of acephate residues. *Pardue et al.* [3] have published the method for the determination of residues of acephate and some other organophosphorus pesticides based on the general *Storherr* method [4]. A multiresidue method has been published [5] which can be used for the g.l.c. analysis of acephate and methamidophos. Because of the polarity of acephate [1, 6], the choice of proper inert supports and stationary phases for

obtaining optimum parameters at the g.l.c. analysis of acephate is most important. The analytical conditions and the evaluation of the method are described in the present paper.

Experimental

A gas chromatograph Fractovap, model 2400T (C. Erba, Milan) equipped with FID, Speedomax XL 681 recorder (Leeds and Northrup, USA), and computing integrator Autolab System IVB (Spectra Physics, USA) was used. The chromatographic conditions were as follows: A glass column 60 × 0.25 cm (i.d.) was packed with 3% of Reoplex-400 (Merck, GFR) on Gas-Chrom Q 100/120 mesh (C. Erba, Milan). The column temperature was 448 K and the injection port and detector temperatures were 458 K. Gas pressures were: carrier gas — nitrogen 85 kPA, hydrogen 60 kPa, oxygen 50 kPa.

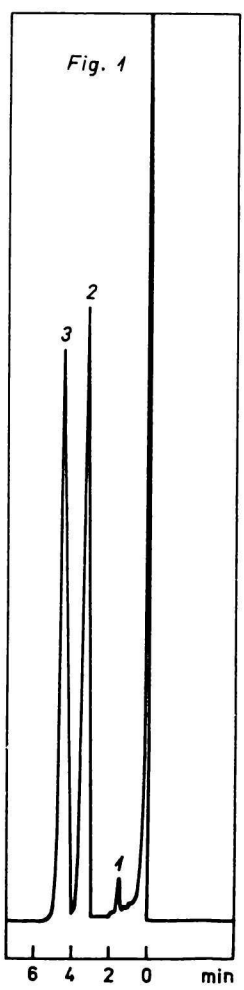
The samples were analyzed by the technique using methyl 2,4,5-trichlorophenoxyacetate (2,4,5-T methyl ester) as internal standard. All the analytical standards: 2,4,5-T methyl ester, *O,O*-dimethyl phosphoroamidothioate, *O,O*-dimethyl *N*-acetylphosphoroamidothioate, acephate, methamidophos, as well as the samples of technical products were supplied by the Research Institute of Agrochemical Technology, Bratislava, Czechoslovakia. A commercial product Orthene® 75 SP (Chevron Chemical company, France) was used for the formulation analysis. Anal. grade chloroform was used as solvent in all cases.

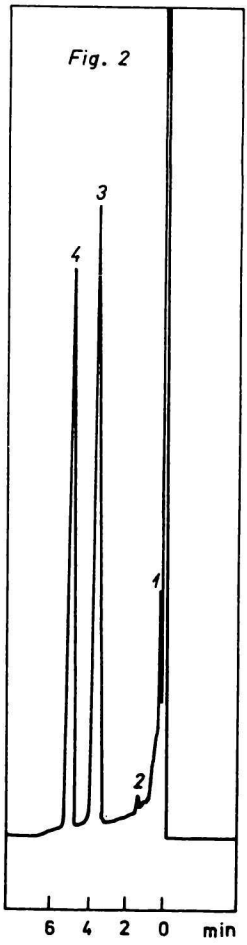
The chloroform calibration solution for acephate determination contained 40 mg of the internal standard (2,4,5-T methyl ester) and 100 mg of the standard acephate in a 10 cm^3 volumetric flask. The chloroform solutions of the technical acephate samples contained 40 mg of the internal standard (2,4,5-T methyl ester) and 120 mg of the technical acephate in 10 cm^3 volumetric flask. A chromatogram of the technical acephate is shown in Fig. 1. The chloroform solutions of the formulated products contained 40 mg of the internal standard (2,4,5-T methyl ester) and 130 mg of the formulated acephate in a 10 cm^3 volumetric flask. Chromatogram of the formulated acephate is shown in Fig. 2. In both cases, only freshly prepared sample solutions were injected onto the chromatographic column.

The chloroform calibration solution for the *O,O*-dimethyl *N*-acetylphosphoroamidothioate determination contained 200 mg of the internal standard (2,4,5-T methyl ester) and 220 mg of *O,O*-dimethyl *N*-acetylphosphoroamidothioate standard in a 10 cm^3 volumetric flask. Freshly prepared chloroform solutions of the technical samples contained 200 mg of the internal standard (2,4,5-T methyl ester) and 250 mg of the technical product in a 10 cm^3 volumetric flask. The chromatogram of the technical *O,O*-dimethyl *N*-acetylphosphoroamidothioate is shown in Fig. 3.

Results and discussion

The accuracy of the method was checked by analyzing the synthetic mixtures. Known amount of the standard of the analyzed compound was weighed along with the known amount of the precursor standard. The results obtained are summarized in Tables 1 and 2.





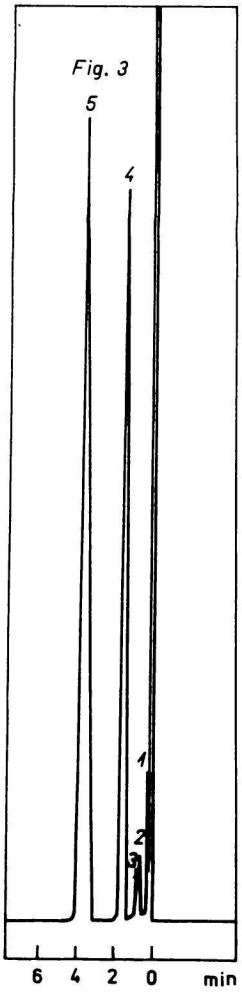


Fig. 1. Technical acephate.
1. *O,O*-Dimethyl *N*-acetylphosphoroamidothioate; *2.* 2,4,5-T methyl ester (internal standard); *3.* *O,S*-dimethyl *N*-acetylphosphoroamidothioate.

Fig. 2. Formulated acephate.
1. Unknown peak; *2.* *O,O-dimethyl N*-acetylphosphoroamidothioate; *3.* 2,4,5-T methyl ester (internal standard); *4.* *O,S*-dimethyl *N*-acetylphosphoroamidothioate.

Fig. 3. Technical *O,O*-dimethyl *N*-acetylphosphoroamidothioate.
1. *O,O*-Dimethyl phosphoroamidothioate; *2, 3.* unknown peaks; *4.* *O,O-dimethyl N*-acetylphosphoroamidothioate; *5.* 2,4,5-T methyl ester (internal standard).

Table 1

Analysis of synthetic mixtures of acephate and *O,O*-dimethyl *N*-acetylphosphoroamidothioate

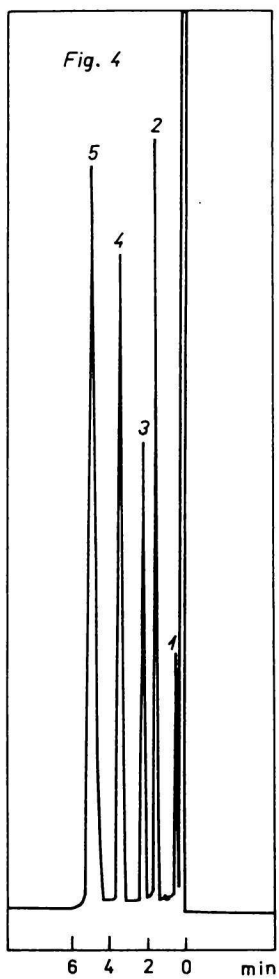
No.	% Acephate		Relative error %
	Weighed	Found	
1	65.87	65.52	0.53
2	75.12	75.34	0.29
3	80.63	80.42	0.26
4	88.55	88.85	0.34
5	90.42	91.20	0.86

Table 2

Analysis of synthetic mixtures of *O,O*-dimethyl *N*-acetylphosphoroamidothioate and *O,O*-dimethyl phosphoroamidothioate

No.	% *O,O*-Dimethyl *N*-acetylphosphoroamidothioate		Relative error %
	Weighed	Found	
1	80.53	80.87	0.42
2	86.42	86.02	0.46
3	91.53	91.20	0.36
4	98.51	99.50	1.02

In searching for optimum chromatographic conditions, we have tested, in addition to the packings mentioned by other authors [2—8], the following stationary phases and solid supports: NPGS, EGS, DEGS, THEED, Reoplex-400, Chromosorb W-HP, Chromosorb G-HP, Gas-Chrom Q. The best resolution of the tested mixture and the most symmetrical peak shapes were obtained with 3% Reoplex-400 on Gas-Chrom Q 100/120 mesh. The optimum temperature conditions were found to be in the range of 393—458 K. All samples analyzed by g.l.c. were simultaneously run on t.l.c. plates, in order to disclose eventual artefacts which might occur due to high column temperature. Silufol precoated plates (Kavalier, Czechoslovakia) were used and visualized by spraying with the DCQ reagent [9]. In the temperature interval investigated no differences were observed between corresponding g.l.c. and t.l.c. records. The method presented here describes the determination of both technical and formulated acephate, as well as the determination of some impurities present in the product. The composition of the mixtures given in Tables 1 and 2 was chosen so as to simulate the samples of



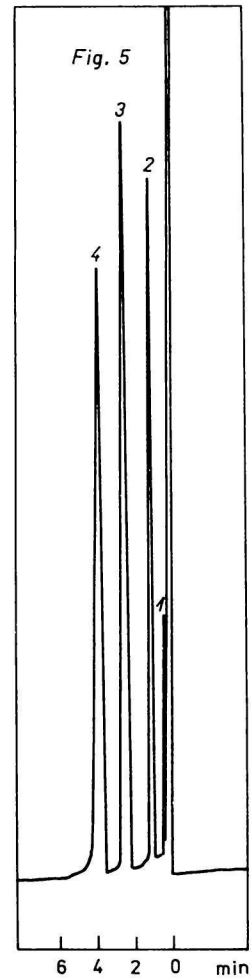


Fig. 4. Synthetic mixture of:
1. O,O-Dimethyl phosphoroamidothioate; *2. O,O*-dimethyl *N*-acetylphosphoroamidothioate; *3. O,S*-dimethyl phosphoroamidothioate; *4.* 2,4,5-T methyl ester (internal standard); *5. O,S*-dimethyl *N*-acetylphosphoroamidothioate.

Fig. 5. Synthetic mixture of:
1. O,O-Dimethyl phosphoroamidothioate; *2.* overlapping peaks of *O,O*-dimethyl *N*-acetylphosphoroamidothioate and *O,S*-dimethyl phosphoroamidothioate; *3. O,S*-dimethyl *N*-acetylphosphoroamidothioate; *4.* di-n-butyl phthalate (internal standard by the method of Carlstrom).

technical acephate prepared by isomerization of *O,O*-dimethyl *N*-acetylphosphoroamidothioate and the technical samples of *O,O*-dimethyl *N*-acetylphosphoroamidothioate prepared by acetylation of *O,O*-dimethyl phosphoroamidothioate. Concentration range was chosen so as to correspond to the concentrations of the analyzed substances in the technical products. The reproducibility of the methods for technical and formulated acephate, as well as for *O,O*-dimethyl *N*-acetylphosphoroamidothioate was evaluated statistically on the basis of analyses of the appropriate products. The results are given in Table 3. From the results obtained it can be seen that the present method is suitable for analysis of the technical and formulated acephate and can be considered equivalent to the method of Carlstrom [2].

The results and the statistical evaluation of the *O,O*-dimethyl *N*-acetylphosphoroamidothioate determination show. that the method is also suitable for analytical control of the technological process in acephate production.

Table 3

Statistical evaluation of the method for analyzed compounds

Sample	$\bar{x}$ %	S.D.	$S_{\bar{x}}$	$\bar{x} \pm t \cdot S_{\bar{x}}$
Technical acephate	69.65	0.60	0.15	69.33—69.98
Orthene 75 SP	74.85	0.54	0.14	74.55—75.15
O,O-Dimethyl *N*-acetylphosphoroamidothioate	91.74	1.24	0.33	91.04—92.44

The last column gives the confidence limits for 95% probability. The data represent the results of 15 repeated determinations of one product.

The resolving power of the chromatographic column is shown in Fig. 4, which is a chromatogram of a mixture of all main impurities along with acephate and the internal standard 2,4,5-T methyl ester. Fig. 5 represents the chromatogram of the mixture shown in Fig. 4 except that di-n-butylphthalate was used as the internal standard instead of 2,4,5-T methyl ester and the mixture was run under the working conditions according to Carlstrom [2].

From Figs. 4 and 5 it can be seen that better resolution of the components of interest was achieved on the column suggested in this paper. Complete resolution of the analyzed mixture to the individual peaks enables direct identification and/or determination of impurities of different toxicological significance.

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