Direct gas-liquid chromatographic determination of cresols in the technical and formulated MCPA

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A gas-liquid chromatographic method is presented for direct determination of 4-chloro-2-methylphenol, 6-chloro-2-methylphenol, 2,4-dichloro--6-methylphenol, and 2-methylphenol in technical products and formulations of 4-chloro-2-methylphenoxyacetic acid. The analysis is performed on a column packed with 5% OV-17 on Chromosorb G, 60—80 mesh, without preliminary extraction and/or derivatization of the samples.

Описывается газо-жидкостный хроматографический метод прямого определения 4-хлор-2-метилфенола, 6-хлор-2-метилфенола, 2,4-дихлор-6-метилфенола и 2-метилфенола в технических продуктах 4-хлор-2-метилфеноксиуксусной кислоты. Анализ проводится на колонке Хромосорба G, 60—80 меш с 5% OV-17 без предварительной экстракции и видоизменений образцов.

Damages to the environment may be caused not only by metabolites of the active ingredients of the pesticide formulations but also by impurities present in technical products of pesticides, having potential effects which vary from acute toxicity to the depreciation of the foods to be protected (taste, taint, appearance). The need for improvement of the complex analytical methods for the technical products of biologically active compounds has become evident in the recent years, mainly for the pesticides that have been introduced into plant protection practice many years before the rapid development of the modern analytical methods.

The herbicide formulations of 4-chloro-2-methylphenoxyacetic acid (MCPA) have been widely used for about forty years. Analytical methods for the active ingredient, the above-mentioned acid and accompanying acids are profoundly worked out and are based mainly on gas-liquid chromatography after derivatization of the samples [1, 2]. However, little attention is paid to the analysis of the MCPA herbicides for the content of phenolic compounds.

Acute toxicity of the chlorocresols from the group of MCPA precursors is relatively low [3]. However, these compounds possess typical disinfectant taint manifest even at very low concentration levels. Thus, chlorocresols are serious potential environmental pollutants causing the degradation of the sensory qualities

of foods. *Dietz* and *Traud* [4] reported the most intensive taint of aqueous solutions from among 126 phenolic compounds tested for monochlorophenols. *Patterson* [5], *Patterson et al.* [6], and *Griffiths et al.* [7] identified 6-chloro-2-methylphenol as the originator of a typical disinfectant taint in meat and biscuits. *Griffiths et al.* [7] determined the taint threshold levels 0.1 ng/g flour for 6-chloro-2-methylphenol and 3.0 ng/g flour for 4-chloro-2-methylphenol. Both compounds are potential impurities in MCPA products.

Land et al. [8] developed a gas-liquid chromatographic method for direct determination of the phenolic compounds in MCPA products but the method is not suitable for commercial formulations. The so far common and widely used method for the determination of the cresols in MCPA products and formulations is the nonspecific colorimetric 4-aminoantipyrine method recommended by FAO and CIPAC experts [9, 10].

The present paper could be of help in solving the problem of the relevance of presence of the individual substituted phenols in the technical products and formulations of MCPA from the aspect of their possible influence on the quality of the plants protected.

Experimental

Standards of 2-methylphenol, 6-chloro-2-methylphenol, 2,4-dichloro-6-methylphenol, 4-chloro-2-methylphenol as well as standards of 2-methylphenoxyacetic acid, 6-chloro-2-methylphenoxyacetic acid, 2,4-dichloro-6-methylphenoxyacetic acid and MCPA were prepared and tested for purity to give single peaks on the gas chromatographic column. The reliability of the method was tested on the commercial MCPA preparations and technical products. All other chemicals used were anal. grade.

Gas chromatograph, type Fractovap 2400 T (C. Erba, Milan) home-modified to enable independent injection port and/or detector body heating regulation, equipped with FID, and computing integrator, type Autolab IVB (Spectra-Physics, USA) were used. The content of phenolic substances was determined by the calibration curve technique. Glass column 300 × 0.2 cm i.d. packed with 5% OV-17 (Applied Science, USA) on Chromosorb G, 60—80 mesh (C. Erba, Milan) was used. The temperatures of the injection port and detector were 473 and 523 K, respectively. The oven was run under two temperatures: A. isothermal 423 K and B. programmed temperature; first at 423 K for 18 min, then heated at the rate of 30 K min^{-1} to 543 K held 12 min. Carrier gas — nitrogen, flow rate 19 $cm^3 min^{-1}$, hydrogen flow rate 38 $cm^3 min^{-1}$, and air flow rate 400 $cm^3 min^{-1}$.

Calibration solution

2-Methylphenol (10 mg), 6-chloro-2-methylphenol (10 mg), 2,4-dichloro-6-methylphenol (10 mg), and 4-chloro-2-methylphenol (50 mg) dissolve in acetone (6 cm^3) and the volume is made up with diluted HCl ($c_{HCl} = 1 \times 10^{-1}$ mol l^{-1}) to 10 cm^3. 2 mm^3 of the solution are injected onto the column.

Technical product solution

10 g of the homogenized sample dissolve in acetone (60 cm^3) and the volume is made up with diluted HCl ($c_{HCl} = 1 \times 10^{-1}$ mol l^{-1}) to 100 cm^3. 2 mm^3 of the solution are injected onto the column.

Formulation solutions

A portion corresponding to 10 g of the technical product is converted to free acids and phenols with HCl ($c_{HCl} = 5$ mol l^{-1}). Acetone (60 cm^3) is added and the volume is made up with diluted HCl ($c_{HCl} = 1 \times 10^{-1}$ mol l^{-1}) to 100 cm^3. 2 mm^3 portions of the solution are injected onto the column.

Injection mode: XY XY, where X — calibration solution injection, Y — sample solution injection.

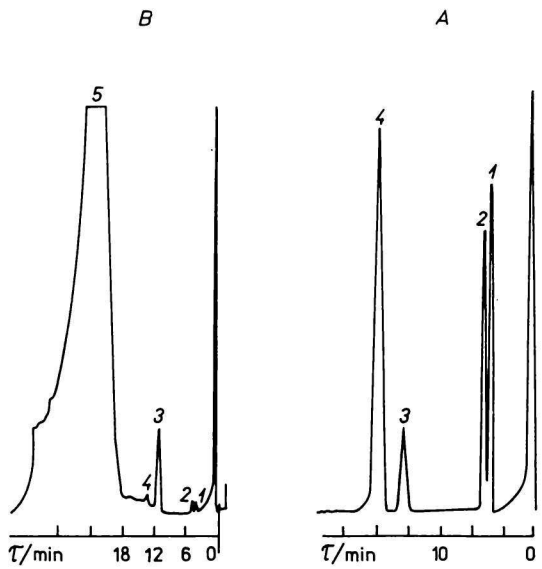

Fig. 1. Chromatogram of sample (*B*) and synthetic mixture (*A*).
1. 2-Methylphenol;
2. 6-chloro-2-methylphenol;
3. 2,4-dichloro-6-methylphenol;
4. 4-chloro-2-methylphenol;
5. total peak of phenoxyalkanecarboxylic acids.

First three injections in the series are chromatographed at oven temperature *A*, the fourth run in the series under the temperature program *B*. The average value of the two subsequent runs is substituted in the formula for the calculation of the individual compound content. Fig. 1 shows the chromatogram of the sample solution run under the programmed temperature *B* and the chromatogram of the calibration solution run under the temperature *A*.

Results and discussion

Because of the lack of modern analytical methods dealing with the problem of phenolic substances in MCPA-based herbicidal products, great attention was devoted to the evaluation of the accuracy of the method presented. The following factors which may cause artefacts in the determination of phenolic substances were evaluated: 1. possible influencing of the content of cresols by the free acids present in the sample, due to their potential heat destruction in the injection port and/or on the column; 2. further possible changes in the content of cresols after the technological conversion of the technical acids to the salts and repeated precipitation of the free acids and phenols.

The accuracy of the method with respect to the different free acids content is given in Table 1 which summarizes the results of the analyses of two mixtures

Table 1

Determination of the cresol content (mass %) in the mixtures with respective phenoxyalkanecarboxylic acid standards

Sample	2-Methylphenol	6-Chloro--2-methyl-phenol	2,4-Dichloro--6-methyl-phenol	4-Chloro--2-methyl-phenol
1 added	7.92	10.98	11.07	10.03
found	8.30	10.74	11.23	9.94
2 added	0.15	0.17	0.17	0.56
found	0.14	0.17	0.14	0.52

prepared by weighing the standards of cresols together with the standards of the corresponding acids. The results obtained did not confirm the suggested possibility of influencing the cresol content by the heat deterioration of the free acids present in the sample in pure form, even at their different concentration levels.

Further possible artefact, namely the influence of the sample treatment on the cresol content, was evaluated on a technical MCPA sample which was previously analyzed for cresol content by the 4-aminoantipyrine method [9]. The product was melted and divided into three parts. Each part was further divided into two aliquots, the first of each couple being held as control and the second one enriched by weighing the known amounts of the cresol standards of interest. All six samples were then melted to homogenize well and converted to the respective salts by mixing with adequate amount of NaOH, KOH, and dimethylamine aqueous solutions. The resulting samples of the MCPA salts, *i.e.* sodium salt (MCPA-Na),

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Table 2

Accuracy of the method of determination of the cresol content (mass %) in the mixtures of MCPA salts

Sample		2-Methylphenol	6-Chloro--2-methyl-phenol	2,4-Dichloro--6-methyl-phenol	4-Chloro--2-methyl-phenol	Σ g.l.c.	Colorimetric
MCPA-Na	added	0.22	0.18	0.42	3.00	3.82	—
	found	0.21	0.23	0.41	3.10	3.95	5.56
	control	—	0.05	—	0.15	0.20	1.16
MCPA-K	added	0.30	0.24	0.51	2.82	3.87	—
	found	0.29	0.27	0.52	2.90	3.98	5.60
	control	—	0.05	—	0.12	0.17	1.19
MCPA-DMA	added	0.10	0.15	0.20	3.07	3.52	—
	found	0.09	0.20	0.19	3.21	3.69	4.09
	control	—	0.05	—	0.14	0.19	0.50

potassium salt (MCPA-K), and dimethylamine salt (MCPA-DMA) were further treated and analyzed as described in Experimental. Each sample was also analyzed by the 4-aminoantipyrine method [9]. The results are presented in Table 2. The last two columns in Table 2 bring the whole cresol content measured by g.l.c. and 4-aminoantipyrine method [9], respectively.

The results in Tables 1 and 2 show clearly that neither the presence of free acids nor the treatment of the sample causes changes in the proper cresol content. The comparison of the determination of cresols by the g.l.c. and the 4-aminoantipyrine methods shows that the nonspecific colorimetric method does not give reliable results which depend even on the sample form (see the difference between MCPA-Na, MCPA-K, and MCPA-DMA).

The reliability of the method was evaluated by analysis of the technical products and commercial formulations. The results presented in Table 3 represent reliability on probability level 95% of 15 repeated analyses of one sample. A good reliability of the results can be seen even in the range of low cresol concentrations. The samples were chosen randomly.

Table 3

Reliability on probability level 95% for individual determinations of the cresol content (mass %) in technical products of MCPA and formulations

Sample	2-Methylphenol	6-Chloro--2-methyl-phenol	2,4-Dichloro--6-methyl-phenol	4-Chloro--2-methyl-phenol
MCPA technical product	0.082—0.090	0.097—0.107	1.919—1.975	0.185—0.201
MCPA-DMA	0.088—0.098	0.045—0.052	1.125—1.181	0.645—0.670
MCPA-Na	0.020—0.025	0.050—0.055	0.084—0.092	0.052—0.060

The temperature program *B* is used at the fourth injection in each XY XY series to purge the free acids which do not release the column at the temperature of 423 K. This mode of injection technique does not influence the accuracy and reliability of the method but saves the time needed for analysis of one sample.

In spite of the effort made there is no reliable evidence yet of the relevance of the level of individual phenolic substances in the MCPA products from the aspect of hygiene and toxicology. *Land et al.* [8] make a distinction between total and free volatilisable phenols on the basis of the difference in the results of direct g.l.c.

analysis of the technical MCPA acetone solutions and sublimate analysis of the vacuum-sublimated solid sample. However, this approach does not include the possible time-depending changes (caused by humidity, pH, temperature, light emission) of the sample. The present method could give a real picture of the content of phenolic substances in the sample, independent of the form or the fate of the sample. Thus, there is a reasonable ground to suggest that the present method could contribute to solving the analytical problem of the substituted phenols in the MCPA products. The method also suits for the analysis of phenolic substances in other phenoxyalkanecarboxylic acid herbicides, *e.g.* MCPP.

Under the conditions described in Experimental it was possible to analyze minimum 0.01% of 2-methylphenol and 6-chloro-2-methylphenol; 0.02% of 2,4-dichloro-6-methylphenol and 0.02% of 4-chloro-2-methylphenol in the samples.

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