EXAMINATION OF CONDITIONS FOR THE DETERMINATION OF CARBAMATE PESTICIDES IN SOILS

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The procedure for the determination of carbamate pesticides in soil was optimized. The following factors affecting the final results were investigated: extracting solvent, extraction procedure, extract purification procedure, and soil type. Triple extraction with acetone and purification of the extract on a two-stage purification column containing an activated carbon–silica gel 1+1 mixture were found optimal. The extracts after treatment were analyzed by RP-HPLC with UV detection. The method developed allows carbamate pesticides in soil to be determined at concentrations in excess of 30 μg kg^{-1}.

Procedures for the isolation of pesticides from soils usually involve extraction with organic solvents. Since ballast substances are co-extracted, the extracts must be successively purified. This can be done by re-extraction with various solvents, repeated evaporation of the extract and successive dissolution, sorption on suitable sorbents, etc.; the methods can also be combined. When applying the sorption approach, either the interferents are sorbed while analytes pass through, or vice versa; the latter approach also involves preconcentration of the analytes.

Extraction and purification procedures for pesticides in natural samples have been described in publications by Walters[1], Ambrus and Thier[2], Steinwandter[3,4] and others[5,6]. Extractants for carbamate pesticides mostly include acetone[7], methanol[8] and ethyl acetate[9], their mutual mixtures[10] and mixtures with water[11]. Among sorbents which are well suited to the purification of carbamate pesticide extracts are Florisil[12], silica gel[13], Nuchar Attaclay[14], Separon SI C18 (ref.[15]), and other single[16] and combined[17] sorbents. A review of this topic can be found in ref.[18].

The aim of this work was to develop a method for the determination of low concentrations of carbamate pesticides in soils. Emphasis was placed on the extract purification procedure as well as on the choice of solvent and extraction procedure. The effect of soil composition on the results of determination was also investigated. The extracts were analyzed by RP-HPLC with UV detection.

EXPERIMENTAL

Apparatus and Chemicals

Chromatographic analyses were performed on a PU 4002 liquid chromatograph equipped with a variable-wavelength UV detector (Pye Unicam, U.K.). A Separon SGX-C18 5 μm column 150 mm long, 3.3 mm i.d. (Tessek, Czechoslovakia) was used. Samples were purified on a multiextractor (Military Repair Enterprise 084, Olomouc, Czechoslovakia) interfaced to an analytical pump (Zeiss, Germany).

Solvents: methanol and acetone for UV, chloroform, ethyl acetate, diethyl ether, all of reagent grade purity and purified in the laboratory; distilled water, purified in the laboratory on a Separon SGX-C18 5 μm column 150 × 3.3 mm i.d. (Tessek, Czechoslovakia).

Adsorbents: silica gel L 100/160 μm for chromatography (Lachema, Czechoslovakia), activated carbon, CARB I and CARB II macroporous carbon sorbents 1 600 and 400 $m^2 g^{-1}$ specific surface area, respectively (Institute of Polymers, Slovak Academy of Sciences, Bratislava).

Pesticides: Carbaryl (Union Carbide Europe, Geneva, Switzerland), carbofuran (FMC Chemicals, Geneva, Switzerland), desmedipham and phenmedipham (Schering, Berlin, Germany).

Procedure

Sample treatment. Sample was dried at a temperature below 40 °C, coarse mechanical impurities (stones, roots) were removed, and the soil was homogenized by crushing and sieved; 50 g portion of the sample was taken for analysis.

Model samples. To a 50 g soil sample pretreated as given above were added 7 – 13 μg of carbamate pesticides in the form of their methanolic solutions (0.1 μg ml^{-1}). Soil was shaken and solvent was allowed to evaporate freely.

Extraction. Soil sample was triply extracted with 50, 20 and 20 ml of the extracting solvent of choice for 15, 10 and 10 min, respectively. After each extraction the extract was collected by filtration.

Extract purification. The combined extracts were evaporated in a vacuum drier. The residue was taken up with 3 × 0.8 ml of acetone and transferred quantitatively on a two-stage purification column which had been washed with 2 × 3 ml of acetone and dried. The extract was sucked through at a flow rate of about 1 ml min^{-1} and the eluate was collected. After sucking the samples, 3 ml of acetone were sucked through the sorbents and the eluate was also collected. The combined eluates were evaporated to dryness, the walls of the vessel were rinsed with 4 × 100 μl of acetone, and the solvent was vacuum evaporated. The resulting residue was dissolved in a defined volume (40 to 100 μl). An aliquot (20 μl) was injected on the chromatographic column.

Chromatographic analysis was accomplished using a Separon SGX-C18 column and a methanol–water 64 + 36 (v/v) mixture as the mobile phase at a flow rate of 0.4 ml min^{-1}; the detection wavelength was 220 nm.

RESULTS AND DISCUSSION

The procedure developed is a result of tests in which various ways of sample treatment were examined. Attention was paid to the extracting agent, extraction procedure, extract purification, the entire purification procedure as well as the pure extract treatment.

In the first step, procedure (*A*) was tested: triple extraction with acetone was performed (50 + 20 + 20 ml, extraction for 15, 10 and 10 min, respectively), to the

combined extract were added a 2% aqueous solution of Na_2SO_4 and dichloromethane (volume proportions 1 + 3 + 0.5), the whole was shaken for 5 min, the organic phase was separated, 2 × 5 ml of dichloromethane were added to the aqueous phase and the mixture was shaken for 3 min. The combined organic phase was evaporated to dryness, the residue was dissolved in 40 μl of methanol, and 20 μl of this solution was injected on the liquid chromatograph column. The chromatogram is shown in Fig. 1 (broken line). With regard to the high background, purification of the combined organic phase on a sorption column of 0.5 g of silica gel was tested; the ensuing sample treatment was as above (procedure *B*). The chromatogram is shown in Fig. 1 (full line).

In another sample treatment procedure (procedure *C*), triple extraction with acetone was applied as above, the extract was evaporated to dryness, and the residue was dissolved in 5 ml of chloroform and sucked through a purification column packed with 0.5 g of silica gel. The sorbent was dried with air stream, 3 ml of distilled water were sucked through the column (not collected), the sorbent was dried again, and elution with 3 ml of acetone was performed. The eluate was evaporated to dryness, dissolved in 2 ml of diethyl ether, about 5 mg of activated carbon were added to the solution, and the whole was allowed to stand in a closed vessel for 20 min with occasional shaking. Thereafter the system was filtered, the filter paper was rinsed with acetone, the combined filtrates were evaporated to dryness, and the residue was taken up in 40 μl of methanol. A 20 μl aliquot was injected on the chromatographic column.

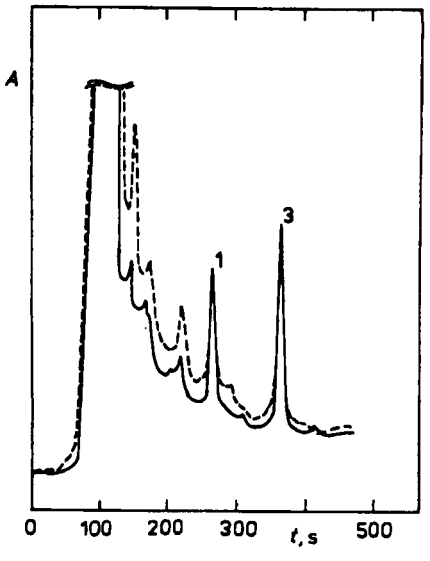

FIG. 1
Chromatograms of extracts from soil containing carbamate pesticides, obtained by procedures *A* (broken line) and *B* (full line). Pesticide: 1 carbofuran, 3 desmedipham

The results indicate that purification of extracts on silica gel lowers the background which is mostly contributed to substances more polar than the analytes. Treatment of the acetone extract with dichloromethane and water (procedures *A* and *B*) did not afford the expected results. The higher recovery in procedure *C* as compared to procedures *A* and *B* indicates that the acetone extracts should preferably be purified by evaporation and subsequent dissolution in a suitable solvent in combination with dynamic purification on silica gel; additional use of activated carbon is also convenient.

In a next procedure (*D*), acetone as extractant was replaced with chloroform. The extract was evaporated to dryness, the residue was taken up in 10 ml of diethyl ether, and 10 ml of distilled water was added. After shaking for 3 min, the organic phase was separated off and evaporated to dryness, and the residue was taken up with 40 μl of methanol. A 20 μl aliquot was injected on the chromatographic column. The results indicate that the use of chloroform brings about higher recovery and lower background. Its drawbacks consist in hygienic problems and in the necessity to purify this solvent prior to its application to the extraction.

The recoveries in procedures *A*, *B*, *C*, and *D* were 60 – 68%, 60 – 70%, 65 – 77%, and 72 – 78%, respectively.

For attaining the highest possible recovery while ensuring a sufficient reproducibility of results, a procedure comprising the assets of the procedures tested above was developed. Low-boiling solvents (with regard to the thermolability of carbamates) of medium polarity (polarity index $p = 2.9 - 6.6$) with high solvation properties for carbamate pesticides were chosen for the extraction. The results for the various carbamates are given in Table I. The application of acetone and chloroform to the extraction of the studied mixture of four carbamates gave comparable results. Acetone is given preference in view of the above-mentioned drawbacks of the use of chloroform. Methanol is somewhat less suitable, and ethyl acetate and diethyl ether are unsuitable altogether for the extraction of all the four carbamates; they are only applicable to some of them (carbofuran).

The extracts were purified on a two-stage purification column. In the first stage (carbon sorbents), nonpolar substances were retained, whereas silica gel trapped substances whose functional groups interact with its –OH groups. When activated carbon is used, the nonpolar as well as polar centres of its inhomogeneous surface participate in the analyte–sorbent interactions. The purification effect with the activated carbon–silica gel combination, however, was comparable to that attained with the macroporous carbon sorbent–silica gel combinations. The differences in the specific surface area of the two sorbents, CARB I and CARB II, had no marked effect. Hence, the specific surface area of 400 $m^2 g^{-1}$ is apparently sufficient for the purification of our model samples.

Figure 2 shows the chromatogram of an extract of medium heavy soil contaminated with carbamate pesticides. The sample was treated as given in Experimental.

The reproducibility of results was evaluated for seven 50 g samples containing 7 to 13 μg of the individual carbamate pesticides. Acetone was used for the extraction and

TABLE I
Recovery (%) in the determination of carbamate pesticides in soil using various extracting solvents[a]

Pesticide	Purification procedure[b]	Acetone	Chloroform	Ethyl acetate	Methanol	Diethyl ether
Carbofuran	AC	74.2	78.9	80.0	79.9	82.2
Carbaryl	AC	97.2	93.9	72.2	96.0	84.5
	C-I	99.1	95.3	75.3	97.7	85.1
	C-II	96.3	95.4	74.2	92.0	85.0
Phenmedipham	AC	79.1	80.3	45.8	79.3	47.2
Desmedipham	AC	82.4	85.0	43.2	75.1	48.7
	C-I	82.0	86.1	41.9	76.0	50.4
	C-II	82.0	80.1	40.5	76.4	52.5

[a] An amount of 7 to 13 μg of carbamate pesticides were added to 50 g of soil; [b] component used in combination with silica gel: AC activated carbon, C-I CARB I macroporous carbon sorbent, C-II CARB II macroporous carbon sorbent.

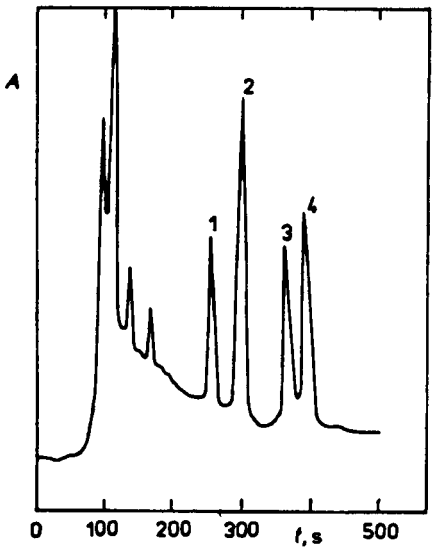

FIG. 2
Chromatograms of extracts from soil containing carbamate pesticides, obtained by optimized procedure (extraction with acetone, purification on a two-stage purification column containing 150 mg of activated carbon + 150 mg of silica gel). Pesticide: 1 carbofuran, 2 carbaryl, 3 desmedipham, 4 phenmedipham

the extract was purified on a purification column containing 150 mg of activated carbon and 150 mg of silica gel (optimized procedure – see Experimental). The recoveries were 74.2 ± 7.3 wt.% for carbofuran, 97.2 ± 3.1 wt.% for carbaryl, 79.1 ± 4.7 wt.% for phenmedipham, and 82.4 ± 3.9 wt.% for desmedipham.

The recovery depends on the soil type because the adsorption properties of soil increase with its increasing organic matter content. Various model soil samples were therefore treated by the optimized procedure, and the recovery was examined. Medium heavy soil alone or with 10 or 30 wt.% sand or with 10 or 30 wt.% peat was investigated. Data given in Table II indicate that addition of sand has a positive effect on the results of analysis, whereas peat, possessing high sorption properties, deteriorates the results or makes the analysis altogether impossible. A well-illustrating example is the analysis of soil taken under a dung-heap; in this case, the background was too high to allow satisfactory results to be obtained. The results did not improve appreciably at purifying the extracts on a two-stage purification column containing 200 + 200 mg of sorbents. For such extreme samples the procedure apparently has to be modified.

Tests of the effect of the soil type on the recovery have been performed previously for atrazine, chlorpropham and triallate[15]. The results of the present tests with four additional carbamate pesticides agree well with those investigations.

The optimized procedure suggested is well applicable to the determination of carbamate pesticides in common soil types. It is convenient owing to its simplicity and relatively low time demands as well as to the high recoveries and good reproducibility of results.

TABLE II
Recovery of pesticides (%) during their analysis by the optimized procedure[a] for various types of soil

Pesticide	Soil				
	Alone	+ 10% sand	+ 30% sand	+ 10% peat	+ 30% peat
Carbofuran	74.2	76.3	76.2	59.0	–[b]
Carbaryl	97.4	99.0	99.1	83.6	–[b]
Phenmedipham	79.1	82.9	82.7	58.2	32.9
Desmedipham	82.4	83.5	84.0	62.3	35.2

[a] An amount of 7 to 13 μg of pesticides per 50 g of soil; soil dried at 40 °C, extraction with acetone, extract purified on activated carbon + silica gel 150 + 150 mg; [b] impossible to analyse.

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