PRECONCENTRATION OF PHENMEDIPHAM AND DESMEDIPHAM BY SORPTION ON SEPARCOL SI C18 T FOR THEIR DETERMINATION IN DRINKING WATER BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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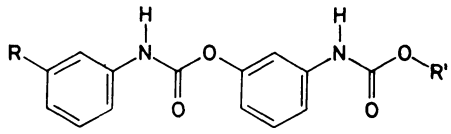
Solvent extraction used routinely for the preconcentration of carbamate herbicides from drinking water was replaced by sorption on the solid sorbent Separcol SI C18 T. Various factors of the preconcentration step that can affect the results of analysis were examined. Real drinking water samples contaminated by phenmedipham were analyzed by RP-HPLC in optimized conditions.

Phenmedipham, [3-(methoxycarbonylamino)-phenyl]-N-(3′-methylphenyl)carbamate, and desmedipham, [3-(ethoxycarbonylamino)-phenyl]-N-phenylcarbamate, are the active components in the commercial agent Betanal(R), used as a postemergent herbicide for the treatment of beet (sugar beet in particular); desmedipham is also present in the agent Betanex(R). The two compounds exhibit a relatively low toxicity to mammals, with $LD_{50} = 3\,000-8\,000$ mg kg^{-1} for phenmedipham and less than 9 600 mg kg^{-1} for desmedipham.



Phenmedipham R = CH_3 ; R' = CH_3
Desmedipham R = H ; R' = C_2H_5

Quantitation of the two carbamate herbicides is complicated by the fact that they are not very stable. An earlier method of determination of phenmedipham in technical substances consists in the TLC treatment on silica gel (F_{254}) using the chloroform–diethyl ether 9 + 1 mixture, combined with reflection spectrophotometric detection at 240 nm. Other methods of determination are based on basic hydrolysis giving rise to *m*-toluidine from phenmedipham and to aniline from desmedipham, their consecutive diazotization and photometric detection, or on their GLC treat-

ment on a stationary phase of 10% PE-SE 30 on Chromosorb G 100S at an injection temperature 235°C, column temperature 180°C and temperature of the ^{63}Ni detector 330°C, the brominated products of the herbicides being subject to analysis. By liquid chromatography, desmedipham is determined on the Permaphase stationary phase at (37·5 ± 0·3)°C using the mobile phase of 1·75% 2-propanol in 2,2,4-trimethylpentane at a flow rate of 2·0 ml min^{-1}; UV detection is employed. All these methods are summarized in monographs[1,2]. A more recent method for the determination of phenmedipham is based on the HPLC/FTIR combined technique[3].

Each partial operation in the determination of the two carbamate herbicides in real samples must be well elaborated. Phenmedipham in drinking water can be determined by HPLC employing solvent extraction for preconcentration[4]. For many substances, the classical solvent extraction can be replaced conveniently by sorption on solid sorbents[5,6]. This approach is tested in the present work for the quantitation of phenmedipham and desmedipham.

EXPERIMENTAL

Apparatus and Chemicals

A PU 4002 liquid chromatograph equipped with a variable-wavelength UV detector (Pye Unicam, England) was used. Columns 250 × 4·6 mm i.d. were packed with LiChrosorb RP 18, 10 μm (Chrompack, The Netherlands). Preconcentration columns contained 1 g of Separcol SI C18 T sorbent (Institute of Polymers, Slovak Academy of Sciences, Bratislava). Phenmedipham and desmedipham were supplied by Schering, W. Berlin. The solvents — acetone and methanol — were of UV grade, distilled water was purified by passing it through a 150 × 3·3 mm i.d. column packed with Separon SGX C18, 5 μm (Laboratorní přístroje, Prague).

Procedure

The carbamate herbicides were sorbed from water on sorption columns packed with Separcol SI C18 T, by pumping with an analytical pump (Carl Zeiss, G.D.R.) delivered as accessory to the SPEKOL 20 instrument. The layout of the apparatus is shown in Fig. 1.

After sucking the whole sample, the column was disconnected from the system and blown with air, and the substances were eluted with acetone. The eluate was collected in polypropylene test tubes equipped with closures. Water was removed with anhydrous sodium sulfate, and the solvent was evaporated in a vacuum drying oven. The walls of the test tubes were rinsed with 0·2 ml of methanol, the solution was evaporated to dryness, and the residue was dissolved in 60 μl of methanol. A 20 μl aliquot of this preconcentrated sample was injected on a column of LiChrosorb RP 18 and eluted with a methanol–water 70 + 30 (v/v), the flow rate being 0·7 ml min^{-1}. The substances were detected at 238 nm.

RESULTS AND DISCUSSION

The sorbents Porapak Q and Separcol SI C18 T (modified silica gel) were tested for

the preconcentration of the herbicides. The latter appeared more suitable, and so all the subsequent experiments were performed with it.

The following factors were examined for optimization of the procedure: shape of the desorption curve, recovery in dependence on the sample flow rate, and dependence on the sample volume. Calibration curves were constructed in the optimized conditions, and the limit of determination was established. Based on the results obtained, real drinking water samples were analyzed.

The desorption curves of the two carbamate herbicides are given in Fig. 2. Solution containing 5 μg of the herbicide in 50 ml of distilled water was poured to the column. After sucking the sample, the column was disconnected from the system and blown with air. The curves for the two substances are similar in shape. Apparently, 1·2 ml of acetone is sufficient for a perfect desorption of the carbamates from the column; volumes of 1·5 ml were actually used.

Fig. 3 demonstrates that for preconcentration columns packed with 1 g of sorbent, flow rates up to 11 ml min^{-1} have virtually no effect on the sorption process or the recoveries established. After surpassing this flow rate limit, the recovery decreases markedly.

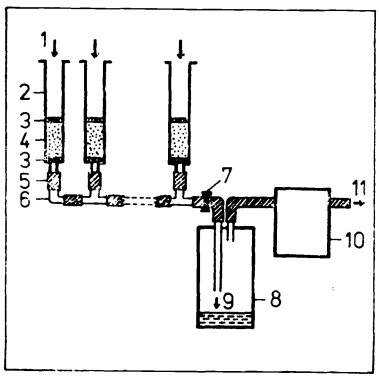


FIG. 1

Layout of the apparatus for the preconcentration of pesticides from water: 1 sample delivery direction, 2 preconcentration column, 3 frit, 4 Separcol SI C18 T sorbent, 5 rubber connection, 6 glass tube, 7 flow rate control, 8 waste, 9 water flow direction, 10 analytical pump, 11 air from the pump

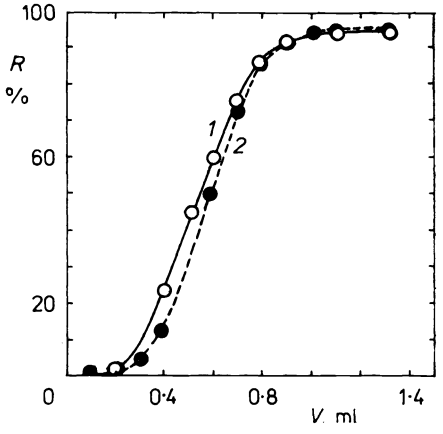


FIG. 2

Desorption curves of phenmediphan (*1*) and desmedipham (2), R recovery, V eluting agent volume. Amounts of 5·0 μg of the herbicide sorbed from 50 ml of distilled water; eluting agent: acetone

Since contamination of drinking water by carbamate herbicides is usually very low, large volumes of sample (1 000 ml) have to be treated. It is conceivable that the sorbed carbamates may be desorbed by this volume of water during the preconcentration. For testing this, water sample containing 5 μg of phenmedipham was forced through the sorbent by suction, and 22 fractions of the passed water, 50 ml volume each, were collected and worked up for the determination of the herbicide in them. Phenmedipham was found in none of the fractions, which gave evidence that even in a volume of 1 100 ml water does not cause desorption of carbamates trapped by the sorbent.

The calibration curves were constructed based on the measurement of 7 samples containing phenmedipham in amounts of 0·66 to 8·28 μg in 50 ml of water, and 7 samples containing desmedipham in amounts of 0·70 to 7·00 μg in 50 ml. The sample flow rate was 2·0 ml min^{-1}, the acetone (1·5 ml) flow rate during the desorption was 1·5 ml min^{-1}.

The calibration dependences were obtained by regression in the form

$$y = (a \pm s_a t_\alpha) + (b \pm s_b t_\alpha)\, x\,. \qquad (1a)$$

The particular forms are

$$y = (-0{\cdot}022 \pm 0{\cdot}095) + (0{\cdot}967 \pm 0{\cdot}019)\, x \qquad (1b)$$

for phenmedipham, and

$$y = (-0{\cdot}060 \pm 0{\cdot}057) + (1{\cdot}002 \pm 0{\cdot}014)\, x \qquad (1c)$$

for desmedipham. The standard deviations characterizing the spread about the regression straight lines are $s = 0{\cdot}124$ and 0·077 and the correlation coefficients are $r = 0{\cdot}9992$ and 0·9996 for phenmedipham and desmedipham, respectively. The recovery of the two compounds was $R = (95{\cdot}73 \pm 2{\cdot}27)\,\%$ and $(97{\cdot}50 \pm 2{\cdot}16)\,\%$, respectively (confidence intervals for $n = 7$). The minimum determinable quantity of the herbicides in drinking water, established by extrapolation, was 0·09 μg l^{-1}.

By way of illustration, Fig. 4 shows chromatograms of model water samples containing the two substances respectively. For optimization of the conditions, each carbamate was analyzed separately.

The procedure was applied to the analysis of water sample from a drinking water source in a region where beet is being produced. The concentration of phenmedipham was calculated by the absolute calibration method and a concentration of $(0{\cdot}77 \pm 0{\cdot}10)$ μg l^{-1} was obtained. The chromatogram of the preconcentrated sample is shown in Fig. 5, demonstrating that peaks of associate substances in the eluate are well separated from the analytical peak.

The preconcentration, purification and chromatographic procedures are so chosen that no unwanted degradation of the carbamates takes place during the workup. The recovery is high and the reproducibility of results is good.

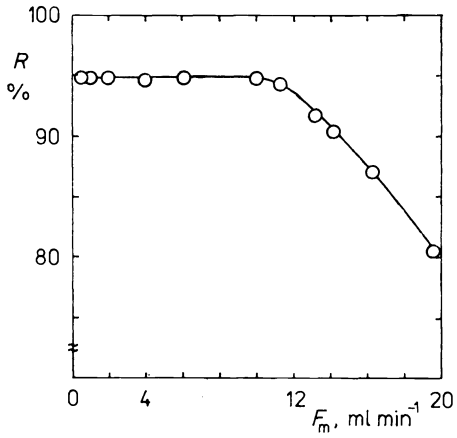


FIG. 3

Dependence of recovery (R) on water flow rate (F_m). Sample: 50 ml of water containing 2·95 μg of phenmedipham

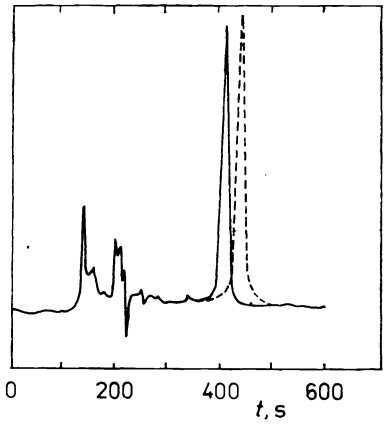


FIG. 4

Chromatograms of model samples of 2·95 μg of phenmedipham (solid line) and 2·80 μg of desmedipham (broken line), both in 50 ml of distilled water

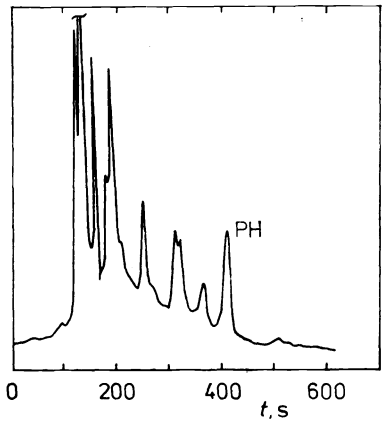


FIG. 5

Chromatogram of a real drinking water sample contaminated by phenmedipham. PH phenmedipham

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