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Simple method for the gas-chromatographic determination of aldicarb, aldicarb sulfoxide and aldicarb sulfone in soil and sugar beets

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Aldicarb is an important carbamate pesticide applied in the protection of plants against sucking insects and nematodes, mainly in the form of the soil pesticide. In soil and plants aldicarb is rapidly oxidized to aldicarb sulfoxide [1–4], which subsequently is slowly oxidized to aldicarb sulfone [5, 6]. Both oxidation products are also extremely toxic to insects and mammalians [5–7].

It was undertaken to study the behaviour of aldicarb and its oxidation products in soil and sugar beets grown in contaminated fields. To simplify the common analytical methods used for the carbamate pesticide determination, a new one was elaborated which applied gas chromatography with AFID to the determination of aldicarb and its oxidation products.

Experimental

The soil samples from the fields were dried under the laboratory's environmental conditions, sieved through a 0.2 mm sieve, stored in glass jars and frozen at −20° C up to the time of analysis.

The sugar beet samples were washed in a stream of water to eliminate soil particles from the beets, then homogenized with a Hobart homogenizer, stored in glass jars and frozen at −20° C up to the time of analysis.

A hundred grams of the soil sample were weighed into an Erlenmeyer flask with glass stopper, mixed with 10 ml of water and left for 1 h to humidify and to deactivate the active centers of the soil. Then 150 ml of ethyl acetate was added and the residues of aldicarb, aldicarb sulfoxide and aldicarb sulfone were extracted by shaking the sample 30 min on a shaker. The supernatant liquid was filtered through a layer of sodium sulphate and the sample was extracted once more for 30 min with 100 ml of ethyl acetate on a shaker and the extract filtered through the same layer of sodium sulphate.

A hundred grams of sugar beet sample were weighed into a wide-necked flask. Then 150 ml of ethyl acetate was added and the sample was left to macerate for 30 min. After that period it was homogenized with an Ultra-turrax homogenizer and the liquid phase was filtered through a layer of sodium sulphate. The extraction of the sugar beet sample was repeated two more times, each time with 100 ml of ethyl acetate.

The combined ethyl acetate extracts were evaporated to about 7 ml on a rotary evaporator at a temperature below 40° C. The concentrated extracts were quantitatively transferred with ethyl acetate into a calibrated tube of 10 ml and the final volume was adjusted with ethyl acetate to 10.0 ml. In this extract the residues of aldicarb were determined. Due to the great volatility of the aldicarb, concentration of the extract to a smaller volume is not possible, causing instantaneous decrease of the recovery. After the aldicarb determination, the extract was quantitatively transferred with ethyl acetate into a roundbottomed flask of 100 ml and rotary-evaporated to a few drops. The residues were quantitatively transferred with ethyl acetate into a calibrated tube of 1 ml and the final volume was adjusted with ethyl acetate to 1.0 ml. In this extract the aldicarb sulfoxide and aldicarb sulfone residues were determined; they differ significantly in their volatility and permit the concentration of the extract up to a few drops.

A gas chromatograph Varian Model 2100 with AFID was used containing tip salt prepared in the laboratory, melted under high pressure with only Rb_2SO_4 in the tip. Prepared in this way, AFID tip salt permits a good reaction for pesticides containing phosphorus and nitrogen in their molecules, and it is characterized by low noise levels [8]. Due to the great volatility of aldicarb it was gas-chromatographed in the 10 ml extracts with a column temperature of 95° C, and aldicarb sulfoxide and sulfone in the 1 ml extracts with a column temperature of 130° C. The GLC column was an U-shaped glass tube 360 cm × 2 mm i.d., packed with 6% OV-210 on Gas Chrom Q 80–100 mesh. Temperatures: detector 270° C, injector 250° C; carrier gas was nitrogen at 30 ml/min; hydrogen at 42 ml/min; air at 340 ml/min. Injection volume: 1 µl.

Results and discussion

The recovery study, the fortification levels and the evaluation of the results obtained of soil and sugar beet samples are presented in Table 1. The recovery study for the samples was carried out taking into account the adsorption and binding processes occurring in nature, for the soil samples in the following way: into an Erlenmeyer flask with a glass stopper 100 g of soil sample was weighed; 1.0 ml of a standard solution of a mixture of aldicarb, aldicarb sulfoxide and aldicarb sulfone at the known levels in ethyl acetate was added. The sample was mixed and left until the next day under laboratory conditions for solvent evaporation and to bind pesticides to the soil constituents. After that period, the samples were extracted as described above. The sugar beet samples fortified with the 1.0 ml of the standard solution mixture were left for 1 h to bind the pesticides with the sample matrix. After that period, the extraction procedure was processed. The recovery of ten repeated analyses exceeded 90%, and the values of standard deviation (SD) and coefficient of variation (V%) were below 10, which indicates good reproducibility and precision of the method. The detection limits for aldicarb and its oxidation products were established for 0.002 mg/kg. Gas chromatograms of the fortified soil and sugar beet samples are presented in Figs 1–4. For the determination, two different temperatures of the GLC column were selected, due to the greater volatility of aldicarb, which needs a lower column temperature (95° C). Moreover, determining first the aldicarb content, an attenuation of 4×10^{-11} was selected, due to the lesser concentration of the pesticide in the extract (10 ml). Then the extract was reconcentrated to 1 ml for aldicarb sulfoxide and aldicarb sulfone determination at a GLC temperature of 130° C, which permitted to decrease the sensitivity of the AFID, selecting an attenuation of 1×10^{-10}. Also, due to the great volatility of aldicarb, it was not possible to concentrate its extracts to 1 ml causing a decrease of the recovery below 50%. Separate determination of aldicarb and its oxidation products in two different concentrations (aldicarb in 10 ml and its oxidation products in 1 ml) provided an excellent recovery for all pesticides.

A rotary evaporator was used for the concentration of the extracts. It was modified by taking out the tube which passes the air through the refrigerant into the round-bottomed flask. In this way the direct spout of air, which produces loss of the residues with the passing air, was eliminated.

The method described is simple and of low cost as compared with others for carbamate pesticide determination [9–15]. It

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Table 1. Statistical evaluation obtained from the fortification study ($n = 10$)

Substances	Fortification levels mg/Kg	Soil		Sugar beets	
		X ± SD	V%	X ± SD	V%
Aldicarb	0.046	94.8 ± 6.4	6.7	93.1 ± 7.2	7.9
Aldicarb Sulfoxide	0.048	90.6 ± 8.9	9.5	90.3 ± 8.8	9.7
Aldicarb Sulfone	0.051	92.8 ± 8.7	9.6	92.0 ± 7.9	8.7

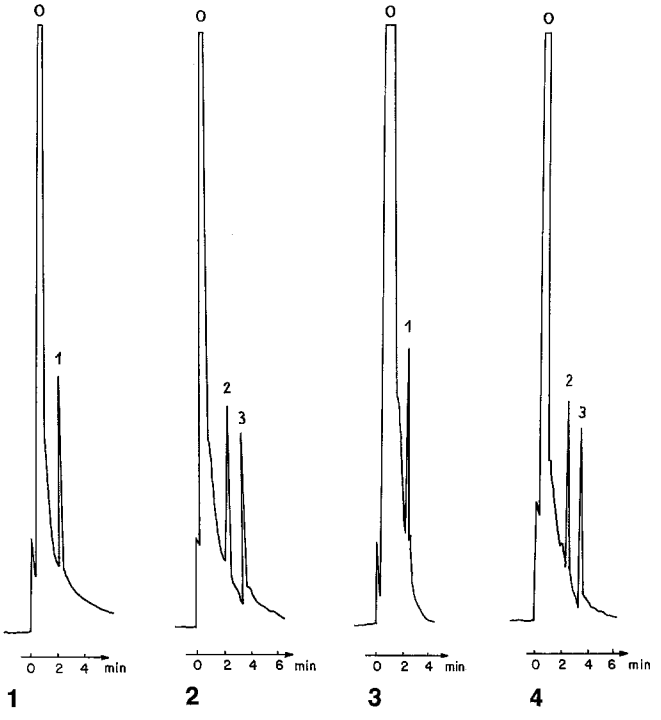

Fig. 1. Gas chromatogram of a soil sample. *0* solvent; *1* 0.46 ng of aldicarb

Fig. 2. Gas chromatogram of a soil sample. *0* solvent; *2* 4.8 ng of aldicarb sulfoxide; *3* 5.1 ng of aldicarb sulfone

Fig. 3. Gas chromatogram of a sugar beet sample. *0* solvent; *1* 0.46 ng of aldicarb

Fig. 4. Gas chromatogram of a sugar beet sample. *0* solvent; *2* 4.8 ng of aldicarb sulfoxide; *3* 5.1 ng of aldicarb sulfone

eliminates clean-up steps of the extracts, but it needs application of a packed GLC column [8, 16]. The shortcomings of the method are contamination of quartz wool in the GLC injection block, which should be replaced after 20–30 injections (each work day). Additionally, the 15–20 cm layer of filling material in the GLC column should be changed after injection of about 100 samples (once a week). But these shortcomings have a lesser significance when compared with the advantages resulting from the elimination of the cleanup steps during the analysis and the excellent recovery obtained.

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