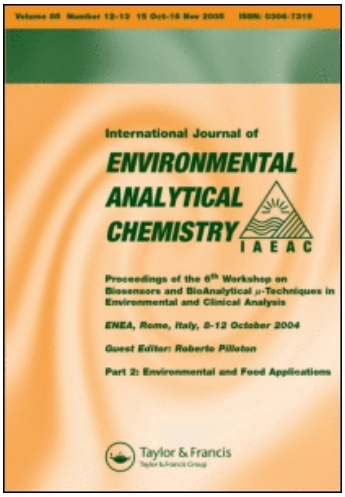

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Analysis of Dichlobenil in Crops and Soils

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Methods for the analysis of the herbicide dichlobenil (2,6-dichlorobenzonitrile) in various crops and soil have been developed. High-pressure liquid chromatography with UV detection can be used to determine dichlobenil at levels down to 0.01 ppm. Dichlobenil can be separated before the final analysis by steam distillation.

A comparison of different analytical methods has shown that the use of a column switching system consisting of a short precolumn as the enrichment column and an analytical column is the most suitable method for obtaining quantitative results with good reproducibility and good recoveries.

KEY WORDS: Dichlobenil, herbicide, crops, soil, trace enrichment, HPLC

INTRODUCTION

The properties of the herbicide 2.6-dichlorobenzonitrile, also known as dichlobenil, favour the use of this compound as total weedkiller and as a herbicide in many different established crops. Its residues are mostly analyzed by gas chromatography (GC) using an electron-capture detector.[1–4] Extracts of crops, soil and also of highly contaminated water samples, however, cannot be determined by GC without some difficult clean-up steps. Beyon *et al.*[1] recommended an oxidation with alkaline permanganate and a steam distillation of

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hexane, followed by extraction as well as thin-layer or column chromatographic operations as clean-up steps.

To avoid such difficult and time-consuming operations we have performed the quantitative determination of the herbicide by HPLC, using different methods of trace enrichment. The high volatility of dichlobenil allows for a steam distillation to separate it from wet interfering matrices. The subsequent enrichment step of dichlobenil from the aqueous solution distillate is possible using HPLC on a C18-bonded phase.[5]

EXPERIMENTAL

Apparatus

Two high pressure pumps M 6000 A (Waters, Königsten, FRG), a variable UV detector SF 770 at 210 nm (Kratos, Karlsruhe, FRG) and an automatic WISP sample processor (Waters) were used. The quantitative evaluation was performed with a HP 3385 A integrator (Hewlett-Packard, Böblingen, FRG).

The determination of trace amounts of herbicide in the ppb range was achieved by either using Sep-Pak cartridges C18 (Waters) or by a two-column switching system with a short enrichment column and analytical column. The columns were switched in an on-line mode by a Rheodyne valve (type 7120) connected to a ten-port Valco valve. Alternatively only a single ten-port Valco valve was used.

As analytical column a stainless-steel column with dimensions of 125 mm × 4.0 mm (Merck, Darmstadt, FRG) was used. A stainless steel column of 17 mm × 4.0 mm (Bischoff, FRG) was used as enrichment column. All analytical columns were packed with good reproducibility with 5 μm LiChrosorb RP 18 (Merck). Enrichment columns were packed with 5 μm Sperisorb ODS (Bischoff). Filtration of the steam distillate was performed by a 5 ml glass syringe connected to a Swinny filter holder (stainless-steel) with a membrane filter of 0.45 μm pore size (both Millipore).

Reagents

All solvents for chromatography were of analytical-grade purity. Acetonitrile for residue analysis and bidistilled water were used for

the mobile phases. HPLC-grade water (Baker, Merck) was used for reconditioning and flushing the enrichment columns and Sep-Pak cartridges, and as solvent for the external standards. For the recovery experiments and the external standards, a herbicide sample of at least 99% purity (Ehrensdoffer, Augsburg, FRG) was available.

Samples

All crops used for recovery experiments were commercially available. Grass samples previously untreated with herbicides, were used. The composition and physical characteristics of the soil used in these studies are shown in Table 1.

Procedures

From crops and soil the active ingredient is separated by steam distillation. The distillate is filtered by membrane filtration. The compound in the filtered steam distillate can be quantitatively determined in several ways by means of HPLC using UV detection at 210 nm as follows:

—direct injection of 0.5 ml steam distillate or
—off-line enrichment using Sep-Pak C18 cartridges, elution with acetonitrile and injection of an aliquot or
—on-line enrichment of 0.5 ml steam distillate by a column switching system.

Extraction by steam distillation

Ground fruit (100 g), e.g., apples, grape, red currants, pears or finely sieved dry earth are transferred into a 500 ml round flask and mixed

Table 1 Characteristics of soil samples

Organic carbon (%)	0.48
Cation-exchange capacity (mval)	4.0
pH-value	6.5
Particle-size analysis (%)	
< 0.002 mm	5.5
0.002 -0.02	2.8
0.02 -0.2	33.5
> 0.2	58.2

with 150 ml bidistilled water. Red currants are further mixed with 150 ml calcium chloride solution to reduce frothing. The generated froth is held back by means of a rising pipe. Steam is introduced through the rising pipe with the aid of a separate pipe equipped with a distribution nozzle. The distillate was subsequently collected by means of a Liebig condenser. The volume in the flask is kept approximately constant by means of additional heating via an external heating element. Exactly 250 ml must be distilled (volumetric flask).

Grass samples (100 g) are transferred into a 1-liter round flask and mixed with 400 ml bidistilled water. Pulverized rice (100 g, 700 μm) is transferred into a 1-liter round flask, mixed with 400 ml bidistilled water, 0.5 g α-amylase, 1.0 g β-amylase and then kept in the sealed flask for 24 h at 35 °C (water bath) to degrade the starch.

The transfer of dichlobenil from the sample to the distillate is shown for water, rice and soil in Figure 1.

In order to transfer 90% of the active ingredient a distillate volume of 100 ml is necessary in the case of rice, 75 ml in the case of soil and 60 ml in the case of water. Essentially quantitative (100%) transfer of dichlobenil is achieved with 250 ml from all matrices.

Cleaning by filtration

Filtration of 30 ml steam distillate is performed with an all-glass syringe connected to a Swinny filter holder with membrane (0.45 μm). The first 10 ml are discarded, the remaining 20 ml are filtered into a sealable air-tight flask.

The sample can then be analysed without further cleaning steps. If analysis cannot take place at once, the sample can be refrigerated for a maximum period of two days.

HPLC analysis

Analysis by direct injection: 0.5 ml of the filtered distillate is injected into a liquid chromatographic system by the WISP sample processor.

Off-line enrichment using Sep-Pak cartridges: A Sep-Pak cartridge is flushed first with methanol and then with bidistilled water. Some of

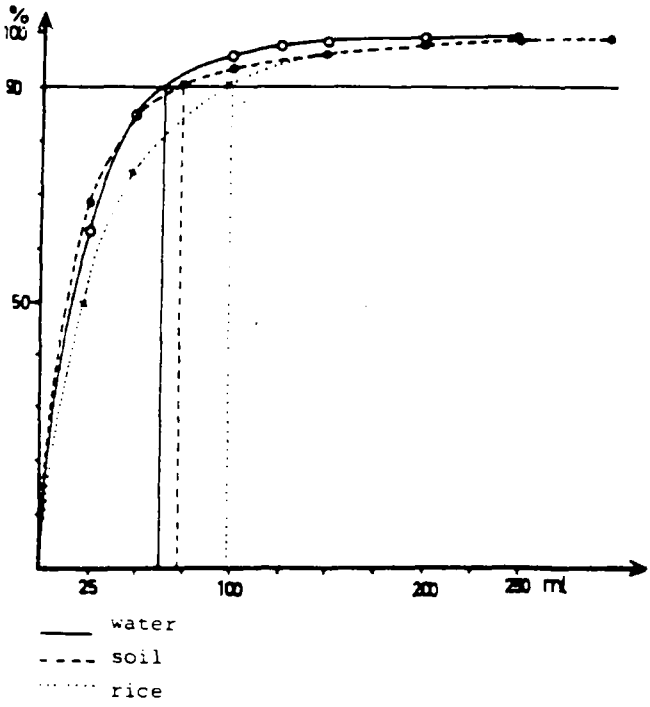

Figure 1 Progress of steam distillation of dichlobenil from water, soil and rice.

the sample (25 ml) is infused at a rate of 5 ml/min. Acetonitrile eluate (2 ml) is removed into a 10 ml measuring cylinder and mixed with 2 ml water. Some of this mixture (40 μl) is injected into the liquid chromatograph by the WISP sample processor.

On-line enrichment by column switching: Trace analysis of dichlobenil can also be performed by column switching.[5] This method has already been described for some other compounds.[6,7] A short pre-column is used as enrichment column which can be switched to the analytical column in an on-line mode by the use of two switching valves. A schematic diagram of the analytical determination is shown in Figure 2.

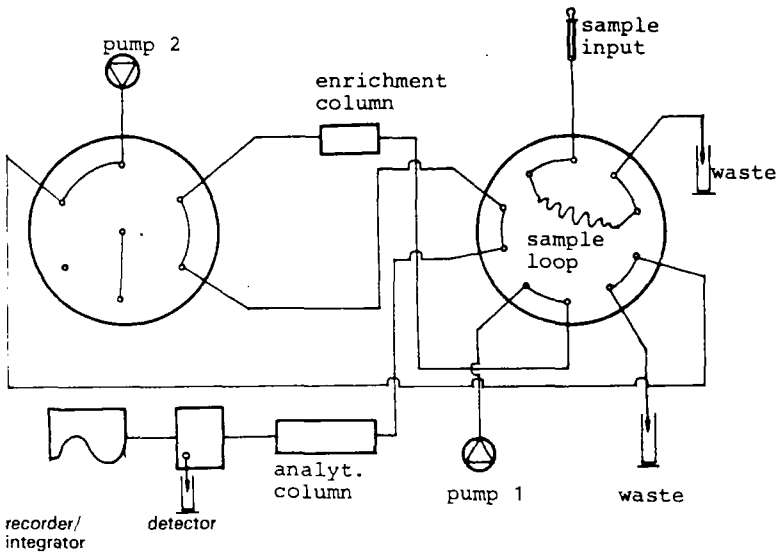

Figure 2 On-line enrichment with precolumn conditioning.

The sample is first injected into a 0.5 ml loop. Both valves are now switched to the second position, so that the precolumn is flushed with bidistilled water (pump 2) and is so reconditioned for enrichment with aqueous solution. The six-port valve must now be switched back. The sample is transferred from the loop to the precolumn by 2 ml water (pump 2) and the dichlobenil is adsorbed onto the RP-18 phase. The analytical determination is started by the switching of the ten-port valve. In this position the herbicide is transferred to the analytical column by the mobile phase (pump 1). The next sample can be injected into the loop during this phase. A more simple method of on line enrichment is shown in Figure 3.

Here only one 10-way Valco valve is needed, but reconditioning of the enrichment column with water before starting the enrichment process is not possible. With this system the dichlobenil peak is only slightly wider, but there are no losses by breakthrough effects.

RESULTS AND DISCUSSION

Recoveries and statistical parameters for the described analytical methods are shown in Table 2. Comparison experiments carried out

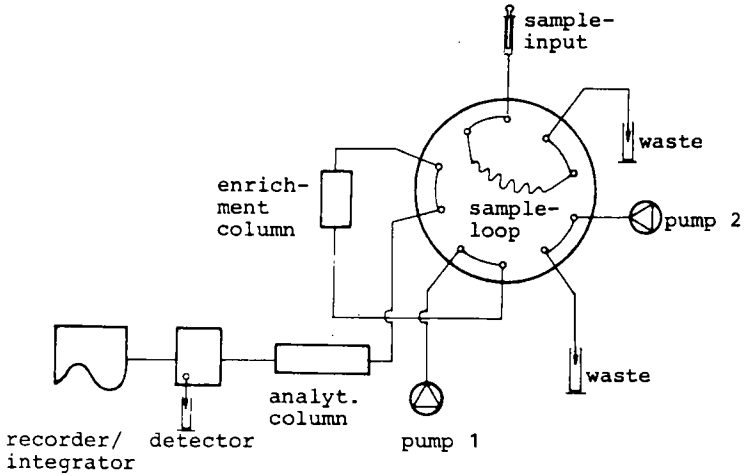

Figure 3 On-line enrichment without precolumn conditioning.

Table 2 Recoveries and statistical parameters for three different analytical methods of dichlobenil in apples

Addition (ppm)	*Range of net recoveries N (%)*	*Mean net recoveries N (%)*	S_1 (%)	S_w (%)
0.5 direct	92.3– 94.3	93.0	1.07	
Sep-Pak	88.7	88.7	0.88	
on-line	97.1– 99.5	98.3	0.90	
0.2 direct	99.3–105.3	102.3	2.35	
Sep-Pak	88.8–104.3	96.1	2.53	
on-line	100.0–102.2	100.1	2.70	
0.1 direct	89.2–102.1	95.2	1.34	4.22
Sep-Pak	88.5– 97.1	93.6	1.50	3.50
on-line	84.1– 94.0	91.0	0.74	2.89
0.05 direct	85.15–94.5	89.8	3.89	
Sep-Pak	87.4– 89.6	88.5	5.70	
on-line	95.4– 88.5	91.4	4.7	
0.01 direct	87.5– 93.8	90.7	4.42	
Sep-Pak	76.6– 93.73	85.2	8.8	
on-line	74.3– 84.3	79.3	5.5	

with the apples show that the mean net recoveries lay between 79% and 102%. The direct injection method gave the highest recovery results, the Sep-Pak off-line enrichment method the lowest. Standard deviation S_1% is lower in the first method than in the second.

The standard deviation S_w% of several ($n=6$) analysed samples with an added amount of 0.1 ppm is most favourable for the on-line enrichment method.

The useful life of the analytical column is low using the direct injection method, the separation efficiency decreases and column pressure rises. Column deterioration is not observed with the on-line enrichment technique. This method is, therefore, recommended for all further investigations.

Recoveries and statistical parameters for on-line enrichment operation of dichlobenil in all matrices (crops and soil) is shown in Table 3.

The mean net recoveries were found to be 83.4% at a concentration of 0.01 ppm and 92.5% at a concentration of 0.1 ppm. As expected the standard deviations S_1% and S_w% increase at lower concentrations. This increase may be attributed to increasing systematic errors and relatively larger matrix interferences at lower concentrations.

The blank values for all materials investigated by means of the on-line technique are included in Table 3. The relatively high S_w% deviation may be expected considering that several types of untreated fruit were analysed and a collective blank value is utilized.

In particular, variable blank values for different grape types were observed. For example the blank value for muscadines were found to

Table 3 Recoveries and statistical parameters for on-line enrichment operation of dichlobenil on all matrices

Addition (ppm)	*Range of net recoveries N (%)*	*Mean net recoveries N (%)*	S_1 (%)	S_w (%)	*Confidence interval*
0.1	87.9–99.0	92.5	2.80	4.13	3.81 (96.3–88.7)
0.05	80.6–97.7	91.1	4.75	6.35	5.86 (97.0–85.3)
0.01	73.2–95.2	83.4	7.97	10.26	9.47 (92.9–73.9)
0.00	1.6–14.0	4.5*	16.8	66.50	—

*referred to 0.1 ppm.

be much higher than those for grapes. Hence blank values were calculated without the muscadines. The evaluation of all blank values shows, that essentially no interfering substances were detected in any of the untreated materials, even at the low attenuations required for the analysis of the lower concentrations of the herbicide in crops and soil.

The detection limit of dichlobenil in all matrices was calculated according to the method of the Deutsche Forschungsgemeinschaft 8, using all blank values, and found to be 5 ppb.

Table 4 gives a specified survey of obtained recoveries and standard deviation for the investigated matrices in detail.

Figure 4 shows typical chromatograms for the determination of dichlobenil in several matrices mentioned above. The chromato-

Table 4 Recoveries and statistical parameters for on-line enrichment operation in different matrices

Matrix	*Addition (ppm)*	*Range of net recoveries N (%)*	*Mean net recoveries N (%)*	S_1 (%)
Grapes	0.1	98.4– 99.6	99.0	3.5
	0.05	97.6– 97.7	97.7	6.0
	0.01	86.5– 89.8	88.2	6.9
Pears	0.1	93.3– 96.5	94.9	2.91
	0.05	92.5– 93.6	93.1	4.1
	0.01	90.8– 90.5	90.6	1.4
Red currant	0.1	91.8– 92.4	92.1	4.42
	0.05	88.1– 88.7	88.4	4.23
	0.01	70.8– 75.5	73.2	5.56
Rice	0.1	79.3–101.0	88.8	4.9
	0.05	72.2– 87.3	80.6	5.9
	0.01	55.7–102.8	73.2	7.7
Grass	0.1	96.4– 97.4	87.86	0.89
	0.05	83.4– 99.1	89.6	5.04
	0.01	71.6– 97.2	84.4	12.7
Soil	0.1	93.2– 95.0	94.1	2.24
	0.05	94.2– 99.5	86.9	3.25
	0.01	93.3– 97.1	95.2	6.06
Apples	0.5	97.1– 99.5	98.3	0.90
	0.2	100.0–100.2	100.1	2.70
	0.1	84.1– 94.0	91.0	0.74
	0.05	88.5– 95.4	91.4	4.7
	0.01	74.3– 84.3	79.3	5.5

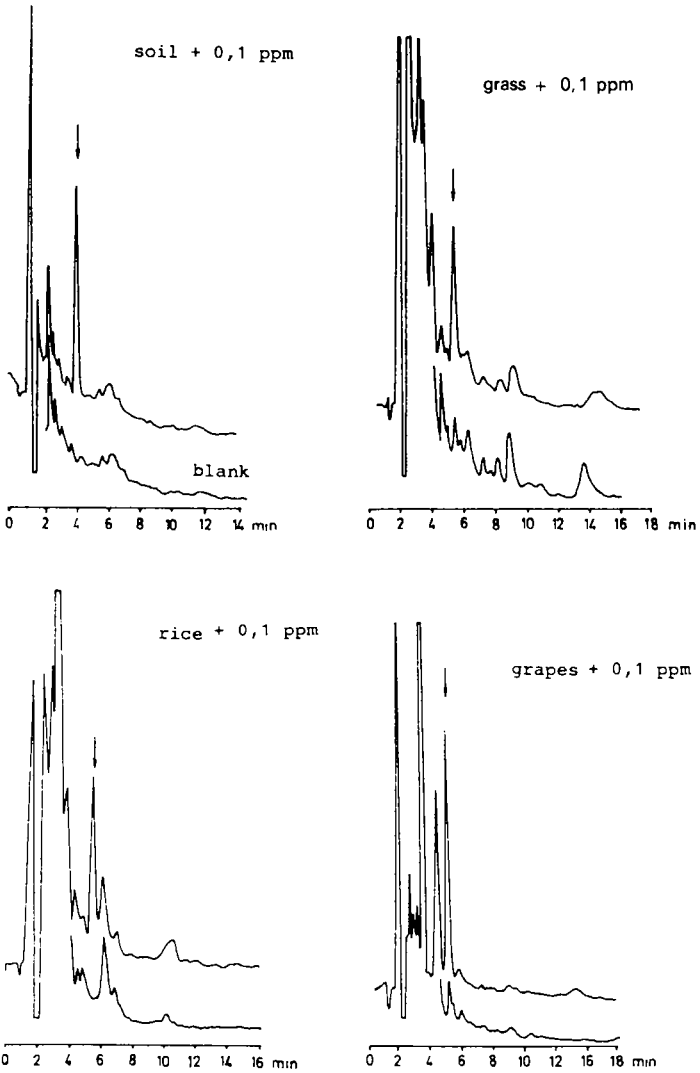

Figure 4 Chromatograms of dichlobenil in different matrices on 5 μm LiChrosorb RP-18, 12.5 × 4 mm, with methanol-water, (70/30), (flow, 1 ml/min), UV detection 210 nm.

grams indicate that using a reversed-phase analytical column a good separation of dichlobenil from remaining UV-active interference with a short run time is possible.

CONCLUSIONS

Steam distillation is a simple and effective method by which dichlobenil can be extracted from crops and soils, followed by quantitative analysis. The described enrichment procedure using precolumn concentration and column switching has proved to be a sensitive HPLC method, so that dichlobenil can be detected in a variety of crops and soils rapidly and accurately. This method gives good results for concentrations down to 0.1 ppm, which is the maximum legally allowed amount of dichlobenil residues in foodstuffs. For concentrations of down to 0.01 ppm a recovery of 70% and confidence interval of 10% is observed.

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