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AUTOMATED GAS CHROMATOGRAPHIC ANALYSIS OF PESTICIDE RESIDUES IN FOOD SAMPLES BY MEANS OF FUSED-SILICA CAPILLARY COLUMNS AND DATA PROCESSING

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SUMMARY

A conventional gas chromatograph with one system for split and splitless injection and one on-column injection system for fused-silica capillary columns and the two selective nitrogen–phosphorus and electron-capture detectors is applied to pesticide residue analysis in food samples. The gas chromatograph is equipped with a two-channel data processor that can be programmed with BASIC. Additionally an autosampler is used with the splitless injector. This automated injection system is connected to a 25-m methylsilicone fused-silica column which is coupled via an effluent splitter parallel to both detectors and used for screening in routine analysis. Calibration is performed on this column by means of three calibration test mixtures which include three internal standards. All compounds are calibrated on both detectors in parallel and the response ratiosis calculated as an additional identification parameter. After the analysis of a of food samples together with the calibration mixture a report is plotted, containing all pesticide residues which may be present in the samples and their tentative quantities. The final confirmation is achieved on the second column, coated with methylphenylsilicone phase, connected to the on-column injector.

INTRODUCTION

Multiresidue analysis of pesticides in food and environmental samples must provide reliable identification and quantitation of a large number of compounds at very low concentrations. Gas chromatography (GC) with the selective electron-capture (ECD) and nitrogen–phosphorus (NPD) detection offers selective detection of contaminants at trace level in the lower ppb range in the presence of a multitude of compounds extracted from the matrix to which these detectors do not respond. The number of compounds used in agriculture for plant protection and the input of pollutants in the environment has increased to the point where it is impossible to separate them all in a single chromatogram even when applying the high-performance capillary columns. Nevertheless GC with ECD and NPD has been established worldwide as the best analytical method for daily food control, contributing very much to the improvement of consumer protection.

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The reliability of identification of any compound is a function of the resolution. Therefore, capillary columns are superior to packed columns for analysing complex mixtures. But until now, capillary GC has been applied to routine pesticide analysis only in a few laboratories.

Early applications of glass capillary columns in food analysis demonstrated their tremendous resolution in the analysis of polychlorinated biphenyl (PCB) isomers and their separation from chlorinated pesticides (CPS) of the DDT group[1,2]. The determination of organophosphorus pesticides (OPS) with glass capillary columns was reported by Krijgsman and Van de Kamp[3] and Hild *et al.*[4]. Stan[5,6] applied glass capillary columns to the analysis of OPS with GC–mass spectrometry (MS), demonstrating the merits of this method for food samples. Several authors reported on the analysis of test mixtures of other chemical classes of pesticides, such as triazines[7], urea herbicides and triazines[8], carbamate insecticides[9] and dinitroaniline herbicides[10]. Some of these examples are included in the catalogues of capillary column suppliers to demonstrate the utility and performance of their products.

Analytical methods developed for pesticide residue determination in food with capillary columns were recently described for CPS and PCBS in milk and dairy products[11] and for chlorophenoxy acid herbicides in flour[12]. An automated analysis of PCB and CPS residues in agricultural products with capillary GC was reported by Tuinstra and Traag[13]. Residue analysis of OPS in food with two-dimensional capillary GC and a flamephotometric detector has been developed by our group[14], and the extension of this method including CP has been reported[15].

In this paper we describe the multiresidue analysis of 95 pesticides in food on two fused-silica columns in a gas chromatograph equipped with two injection ports and two selective detectors (electron-capture and nitrogen-phosphorus) with dual-channel data processing and autosampler.

EXPERIMENTAL

Instrumentation

The GC analysis was carried out on a gas chromatograph HP 5880 A (Hewlett-Packard, Avondale, CA, U.S.A.) equipped with two injection ports for capillary columns and the two selective detectors, electron-capture and nitrogen–phosphorus. One injection port is designed for splitless injection, the other for on-column injection. Both injection ports were supplied by Hewlett-Packard. Our HP 5880 A instrument is equipped with a HP 7671 A autosampler for 36 sample bottles.

Data from the two detectors were processed simultaneously and reported on two separate terminals, one of which was provided with a cartridge tape device.

Installation of capillary columns

One fused-silica capillary column, coated with "bonded phase"dimethylsilicone BP 1 (SGE, Ringwood, Australia), 25 m x 0.2 mm I.D., was connected to the splitless injector; the second fused-silica capillary, coated with "bonded phase" methylphenylsilicone BP 10 (SGE), 12 x 0.2 mm I.D., was connected to the on-column injector. Both columns were joined in an effluent splitter constructed by using fused silver chloride[16]. The ends of the two fused-silica columns, together with two short deactivated fused-silica capillaries (0.2 mm I.D.) connected to the two detectors, were sealed into a glass sleeve.

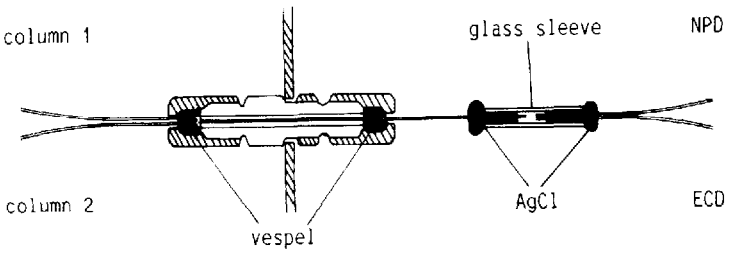


Fig. 1. Effluent splitter.

Recently we modified this splitting device by using the new outlet splitter from SGE (VSOS-123630) shown in Fig. 1.

Gas chromatography

Helium was used as carrier gas and make-up gas for NPD (20 ml/min); the electron-capture detector was purged with 25 ml/min argon and 10% methane. The temperature of both detectors was 300°C and that of the splitless injector was 240°C. The sample volumes were 1 μl for both the autosampler and the manual injection, on both columns. Splitless injection according to Grob and Grob[17] into the "cold" column at 100°C was carried out with the split valve closed 30 sec, on-column injection with a 10-μl syringe and a fused-silica needle at 90°C. One minute after injection, the following temperature program was started: 30°C/min to 150°C; 2 min; 3°C/min to 205°C; 10°C/min to 240°C; 2°C/min to 260°C; 10 min; stop; cool to the initial temperature (100 or 90°C).

Materials

Pesticides were purchased from Dr. Ehrenstorfer, Augsburg, F.R.G., in 97–99% purity. Solvents and chemicals for clean-up of food samples were analytical-grade products of E. Merck (Darmstadt, F.R.G.).

Internal standards for determination with NPD, O-phenyl dimethylthiophosphinate (PT) and O-2-naphthyl dimethylhiophosphinate (NT), were prepared as described[18].

METHODS

Clean-up of food samples

The clean-up followed the methods of Becker[19] and Specht and Tillkes[20]. Internal standards were added to the homoigenized food samples before the first solvent extraction step. The final concentration of the purified extracts was the equivalent of 2 g food in 1 ml.

Automatic GC with data processing

The HP 5880 A chromatograph is provided with a series of prepared integration and calibration methods for chromatogram data processing. The internal standard calibration method including peak recognition with name annotation was used throughout this work.

Using the cartridge tape device, analytical methods can be stored in specified

analysis files. The entire pesticide GC analysis procedure is stored on three separate analysis files, each containing the following information: (a) all instrument settings for producing a chromatogram; (b) two calibration tables, created in parallel for the corresponding pesticide test mixture from the detector signals of ECD and NPD with the internal standard method.

The parameter setting in all three analysis files is identical, whereas the calibration tables correspond to the three calibration test mixtures. After entering sample numbers and names via the alphanumeric keyboard, the automatic analysis is controlled by a BASIC program[21]. The structure of the computer program is outlined in the following scheme.

BASIC program for controlling automatic pesticide analysis in food samples

Calibration

(1) Load analysis file for test mixture I
(2) Perform GC analysis of test mixture I
(3) Recalibration according to actual values
(4) Repeat the calibration procedure (1–3) with other test mixtures

Analysis of samples

(5) Plot all chromatograms on the two channels without analysis report
(6) Save integration data of all samples on tape

Calculation

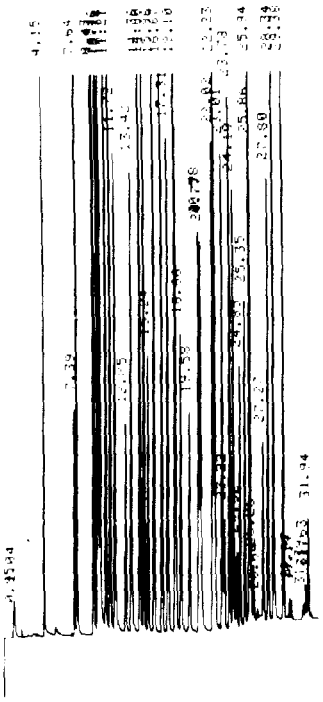
(7) Load integration data of first sample
(8) Load the two calibration tables of test mixture I
(9) Recognition of all pesticides and calculation of concentrations with internal standard method
(10) Comparison of identification and quantitative data of the two channels
(11)Report of results
(12) Repeat steps 8–11 with other test mixtures for first sample
(13) Final report for first sample
(14) Repeat steps 7–13 for each sample.

Examples of printed reports are given in Figs. 7 and 8.

RESULTS AND DISCUSSION

The automatic pesticide analysis with data processing, as described under Methods, is carried out only on the BP 1 column, connected to the splitless injector. The purpose of these GC analyses is to screen the food samples for positive results. A threshold is set after the recognition and quantitation procedure to reject all results giving residue concentrations of less than 10 ppb. The confirmatory analysis for positive results is performed on the BP 10 column by applying on-column injection. This technique is the most adequate one for quantitation in capillary work and for labile compounds. It will be described in detail elsewhere[22].

Pesticide residue analysis, as outlined, requires a daily calibration of the instrument with all pesticides as test compounds. This procedure is indispensable because the whole system must be tested for inertness with all labile compounds. Although calibration for a limited number of substances is a trivial task, it grows to challenging proportions when the analyst must analyze 100 compounds. In Fig. 2, the chromatogram of our test mixture III containing 35 CPS together with the internal standard is



STANDARD MIXTURE FOR HALOGENATED PESTICIDES IN ECD
ISTD

RT	EXP RT	AREA	CAL	AMOUNT	NAME
4.15	4.15	221360.00	1	2.000	DICHLOBEN+*
7.39	7.39	98000.10	2	2.000	CHLORFPROP-M
7.64	7.64	498364.00	3	2.000	TECNAZEN
9.43	9.43	963697.00	4	4.000	ALPHA-BHC*
9.83	9.83	598043.00	5	4.000	DICHLORAN+*
10.16	10.16	581294.00	6	2.000	HCB\BETA-BHC
10.74	10.74	497798.00	7	2.000	LINDAN
11.21	11.21	451890.00	8	2.000	QUINTOZENE
11.72	11.72	391374.00	9	2.000	CHLOROTHALO+
12.85	12.85	143895.00	10	2.000	TRIALLAT+*
13.42	13.42	369687.00	11	2.000	METRIBUZIN+
14.36	14.36	512715.00	12	4.000	VINCLOZOL+*
14.80	14.80	432994.00	13	2.000	HEPTACHLOR+
15.24	15.24	201165.00	14	2.000	DINOSEBACET+
15.86	15.86	496674.00	15	4.000	DICHLOFLUA+
16.67	16.67	449520.00 *	16	ISTD 1	ALDRIN
17.31	17.31	370229.00	17	2.000	CHLORT\TRIAD
18.10	18.10	649985.00	18	4.000	CAPT\NITROTH
18.66	18.66	254893.00	19	8.000	FOLPET+
19.58	19.58	180220.00	20	4.000	PROCYMIDON+*
20.58	20.58	325383.00	21	2.000	ENDOSULF I
20.77	20.77	323497.00	22	2.000	CHLORFENSON
22.02	22.02	396824.00	23	2.000	DIELDRIN
22.23	22.23	451120.00	24	2.000	DDE
23.01	23.01	373064.00	25	2.000	ENDRIN\BUPIR
23.22	23.22	75987.50	26	2.000	ENDOSULF II
23.78	23.78	353502.00	27	2.000	BINAPACRYL+*
24.19	24.19	294392.00	28	2.000	DDD
24.85	24.85	156473.00	29	2.000	TETRASUL
25.35	25.35	185316.00	30	2.000	FENAZAFLOR+*
25.86	25.86	244373.00	31	2.000	DDT
25.94	25.94	397337.00	32	4.000	CAPTAFOL+
27.27	27.27	117109.00	33	4.000	IPRODIONE+
27.80	27.80	239528.00	34	4.000	METHOXYCHL+
28.34	28.34	372273.00	35	4.000	TETRADIFON+
29.38	29.38	433121.00	36	4.000	MIREX
31.94	31.94	67762.00	37	4.000	PERMETHRIN

Fig. 2. Chromatogram by ECD and report of test mixture III on the BP 1 column. RT = Retention time in min; amount in ng.

shown. By application of the sophisticated temperature program, nearly all pesticides and the internal standard can be separated, with the exception of four critical pairs. These critical pairs are represented in the test mixture by only one compound, which is denominated in the report in the first position, followed by a dash and the name of the non-calibrated pesticide. Discrimination between the two compounds is achieved on the second, more polar column. Several pesticide names in the report are followed by a cross. This indicates that these pesticides respond to NPD and must be found in the corresponding report. The coincidence of the recognition and quantitation in both channels is important information about the identity of a pesticide. Comparison of the results of the two channels is carried out by the computer program and reported for each sample (see Figs. 7, 8).

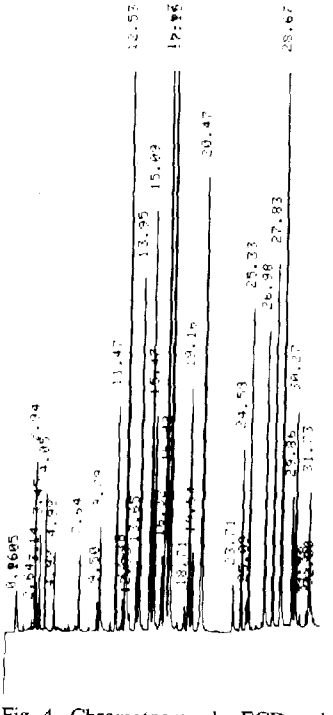
A chromatogram of Test Mixture I, containing 37 OPS together with two internal standards, is shown in Fig. 3.

The record of the NPD signal demonstrates a sufficient separation of these 39 substances on the 25-m BP 1 capillary column. Many of the OPS respond to ECD as shown in Fig. 4. In the reports of both calibration tables, again crosses following the pesticide names are included in order to indicate the response and calibration in the other detector and data channel. Considering the great number of OPS in use, one cannot expect to find any chromatographic system able to separate them all. Therefore, we created a second test mixture (II) including 20 OPS which would form critical pairs

STANDARD MIXTURE I FOR ORGANOPHOSPHORUS PESTICIDES IN NPD
ISTD

RT	EXP RT	AREA	CAL	AMOUNT	NAME
2.29	2.28	4499.20	1	2.000	DIMEFOX
3.43	3.42	414.46	2	2.000	DICHLORVOS++
4.28	4.26	146.90	3	6.000	DIOXATHION+
4.99	4.97	295.07	4	2.000	MEVINPHOS++
5.42	5.45	322.32	5	2.000	PT
6.57	6.54	590.11	6	4.000	DEMEPHION
7.13	7.11	391.02	7	2.000	HEPTENOPHOS+
7.65	7.62	1836.17	8	2.000	THIONAZIN+
7.85	7.83	605.24	9	2.000	DEMETON-S-ME
8.70	8.69	440.66	10	2.000	DICROTOPHOS
9.28	9.26	1458.34	11	2.000	SULFOTEP
9.51	9.48	901.51	12	2.000	PHORATE++
9.80	9.77	1506.04	13	2.000	DIMETHOATE++
10.94	10.91	218.10	14	6.000	DIOXATHION
11.48	11.45	1723.80	15	2.000	FONOFOS+
12.18	12.17	1137.68	16	2.000	DIAZINON++
12.53	12.51	1748.96	17	4.000	FORMOTHION+
12.90	12.89	1159.01	18	2.000	ETRIMFOS+
13.65	13.65	778.18	19	4.000	PHOSPHAMI+
13.96	13.94	1934.59	20	2.000	PARATH-ME++
15.09	15.09	763.34	21	2.000	FENCHLORVOS+
15.47	15.47	1825.60	22	2.000	FENITROTH+
16.32	16.33	927.38	23	2.000	MALATHION+
16.82	16.82	1054.22	24	2.000	PARATHION+
17.15	17.16	1567.42	25	4.000	CHLORTHION+
17.63	17.63	1644.61 +	26	ISTD 1	HT
19.15	19.18	275.85	27	2.000	CHLORFENVIN+
19.53	19.55	1173.74	28	2.000	METHIDATH++
20.48	20.49	1429.64	29	2.000	BROMO-ET+
23.69	23.73	954.47	30	4.000	FENSULFO++
24.56	24.60	1236.76	31	2.000	ETHION++
24.70	24.74	1004.19	32	2.000	TRIAZOPHOS+
25.31	25.35	584.37	33	2.000	CARBOPHENO++
26.96	26.99	1334.33	34	4.000	PHOSMET+
27.81	27.85	531.51	35	2.000	PHENKAPT++
28.64	28.70	1532.84	36	4.000	PHOSALON+
29.82	29.89	1681.72	37	2.000	AZINPHOSETH+
30.22	30.30	1128.31	38	4.000	DIALIFOR++
31.67	31.76	708.64	39	4.000	COUMAPHOS++

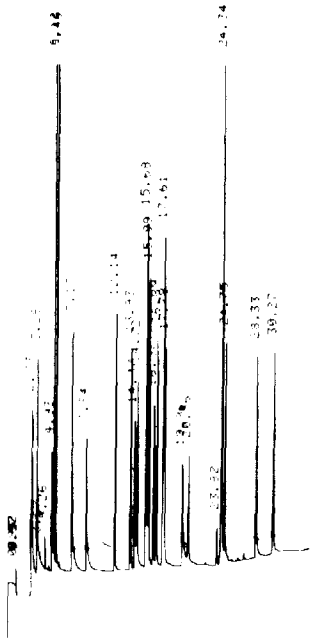
Fig. 3. Chromatogram by NPD and report of test mixture I on the 25-m BP 1 column.



STANDARD MIXTURE I FOR ORGANOPHOSPHORUS PESTICIDES IN ECD
ISTD

RT	EXP RT	AREA	CAL	AMOUNT	NAME
3.45	3.44	26931.30	1	2.000	DICHLORVOS++
4.98	5.00	27155.30	2	2.000	MEVINPHOS++
7.64	7.66	40850.80	3	2.000	THIONAZIN+
9.50	9.52	15925.20	4	2.000	PHORATE++
9.79	9.82	88219.50	5	2.000	DIMETHOATE++
11.47	11.48	144786.00	6	2.000	FONOFOS+
12.18	12.20	23417.50	7	2.000	DIAZINON++
12.53	12.55	466195.00	8	4.000	FORMOTHION+
13.65	13.68	49802.90	9	4.000	PHOSPHAMI+
13.95	13.97	261011.00	10	2.000	PARATH-ME++
15.09	15.11	300473.00	11	2.000	FENCHLORVOS+
15.47	15.50	165759.00	12	2.000	FENITROTH+
16.32	16.35	59711.40	13	2.000	MALATHION+
16.67	16.67	444884.00 +	14	ISTD 1	ALDRIN
16.82	16.85	97279.30	15	2.000	PARATHION+
17.15	17.17	425662.00	16	4.000	CHLORTHION+
19.16	19.19	182273.00	17	2.000	CHLORFENVIN+
19.54	19.56	58946.90	18	2.000	METHIDATH++
20.47	20.49	389298.00	19	2.000	BROMO-ET+
23.71	23.74	39621.80	20	4.000	FENSULFO++
24.58	24.59	183229.00	21	2.000	ETHION++
25.33	25.33	158355.00	22	2.000	CARBOPHENO++
26.98	26.98	164983.00	23	4.000	PHOSMET+
27.83	27.83	178742.00	24	2.000	PHENKAPT++
28.67	28.67	332640.00	25	4.000	PHOSALON+
29.86	29.87	91453.10	26	2.000	AZINPHOSETH+
30.27	30.27	137449.00	27	4.000	DIALIFOR++
31.73	31.73	118603.00	28	4.000	COUMAPHOS++

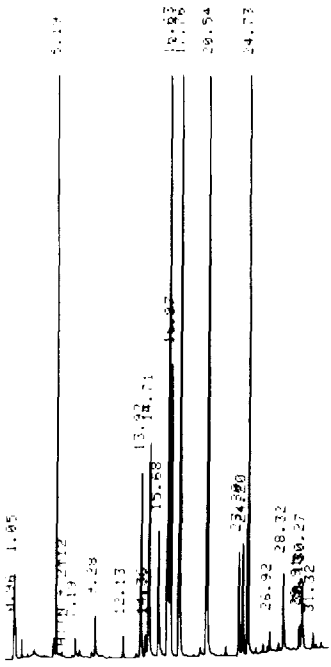
Fig. 4. Chromatogram by ECD and report of mixture in Fig. 3.



STANDARD MI TURE II FOR ORGANOPHOSPHORUS PESTICIDES IN NPD
ISTD

RT	EXP RT	AREA	CAL	AMOUNT	NAME
3.28	3.28	1325.20	1	2.000	METHAMIDO+
4.93	4.93	547.43	2	2.000	ALEPHATE+
5.18	5.18	1936.59	3	2.000	CHLORMEPHOS+
5.46	5.46	1222.02	4	2.000	PT
7.17	7.17	1478.99	5	2.000	OMETHOATE+
8.84	8.84	951.83	6	4.000	MONOCROTOPH
12.14	12.14	1248.81	7	2.000	DISULFOTON++
13.93	13.93	1099.84	8	2.000	DICHLOFENT++
14.37	14.37	960.59	9	4.000	DE-M-SULFON+
14.72	14.72	1095.26	10	4.000	PARAOXON++
15.68	15.68	2107.60	11	4.000	AMIDITHION+
15.99	15.99	1563.23	12	2.000	PIRIMI-ME+
16.57	16.57	851.70	13	2.000	FENTHION
16.89	16.89	1165.10	14	2.000	DURSBAN+
17.61	17.61	1442.62 +	15	ISTD 1	HT
17.78	17.78	1176.51	16	2.000	BROMOPHOS+
19.36	19.36	966.77	17	4.000	VAMIDITHION
20.56	20.56	567.27	18	4.000	TETRACHLRV++
23.82	23.82	151.76	19	4.000	CHLRTHIO I++
24.34	24.34	2889.60	20	2.000	TRIAMIPHOS+
24.75	24.75	946.39	21	4.000	CHLRTHIIII++
28.33	28.33	1233.60	22	4.000	AZINPHOSME++
30.27	30.27	1075.05	23	2.000	PYRAZOPHOS+

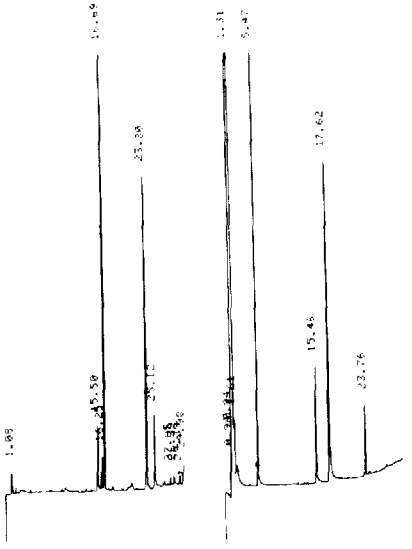
Fig. 5. Chromatogram by NPD and report of test mixture II on the 25-m BP 1 column.



STANDARD MIXTURE II FOR ORGANOPHOSPHORUS PESTICIDES IN ECD
ISTD

RT	EXP RT	AREA	CAL	AMOUNT	NAME
5.19	5.19	84263.10	1	2.000	CHLORMEPHOS+
7.19	7.19	15466.50	2	2.000	OMETHOATE+
12.13	12.13	16503.10	3	2.000	DISULFOTON++
13.92	13.92	137295.00	4	2.000	DICHLOFENT++
14.71	14.71	172411.00	5	4.000	PARAOXON++
15.68	15.68	105982.00	6	4.000	AMIDITHION+
16.63	16.63	440215.00 +	7	ISTD 1	ALDRIN
16.87	16.87	214312.00	8	2.000	DURSBAN+
17.76	17.76	487442.00	9	2.000	BROMOPHOS+
20.54	20.54	454641.00	10	4.000	TETRACHLRV++
23.80	23.80	66937.90	11	4.000	CHLRTHIO I++
24.20	24.20	67989.40	12	4.000	CHLRTHIO II+
24.73	24.73	346170.00	13	4.000	CHLRTHIIII++
28.32	28.32	59199.50	14	4.000	AZINPHOSME++
30.27	30.27	40697.10	15	2.000	PYRAZOPHOS++

Fig. 6. Chromatogram by ECD of mixture in Fig. 5.



REGISTER OF PESTICIDE RESIDUES OF 1 SAMPLE

NO	SAMPLE	NAME	PPM	RT	EXP.RT	REL.R
CALCULATED FROM STANDARD MIXTURE I FOR P- COMPOUNDS						
4	EXAMPLE	PT	.92	5.47	5.47	.311
4	EXAMPLE	FENITROTH*	.43	15.46	15.46	.877
4	EXAMPLE	NT	1.00	17.62	17.62	1.000
4	EXAMPLE	FENSULFO**	.26	23.76	23.64	1.344

THE DIFFERENCE BETWEEN THE DETECTORS AMOUNTS TO 5.94134 %
FOR FENITROTH*
THE DIFFERENCE BETWEEN THE DETECTORS AMOUNTS TO 97.8584 %
FOR FENSULFO**

CALCULATED FROM STANDARD MIXTURE II FOR P-COMPOUNDS

4	EXAMPLE	PT	.96	5.47	5.46	.310
4	EXAMPLE	NT	1.00	17.62	17.62	1.000
4	EXAMPLE	CHLPYRIO I**	1.78	23.76	23.84	1.353

THE DIFFERENCE BETWEEN THE DETECTORS AMOUNTS TO 79.8446 %
FOR CHLPYRIO I**

CALCULATED FROM STANDARD MIXTURE FOR N-COMPOUNDS

4	EXAMPLE	PT	1.03	5.47	5.47	.310
4	EXAMPLE	NT	1.00	17.62	17.62	1.000
4	EXAMPLE	BINAPACRYL**	.84	23.76	23.77	1.349

THE DIFFERENCE BETWEEN THE DETECTORS AMOUNTS TO 8.39152 %
FOR BINAPACRYL**

****

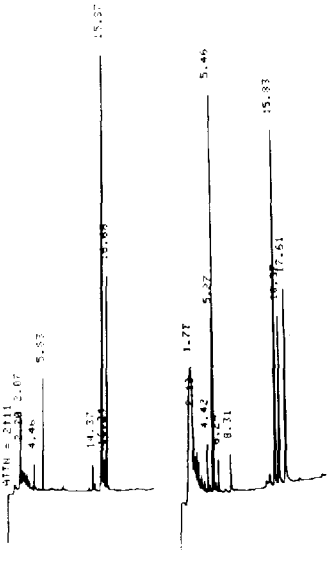
FENITROTH* IS SUSPECTED IN EXAMPLE
BINAPACRYL** IS SUSPECTED IN EXAMPLE

****

* BELONGS TO A CRITICAL PESTICIDE THAT INDICATES SIMILAR RETENTION TIME TO A COMPOUND OF ANOTHER STANDARD MIXTURE

** BELONGS TO A COMPOUND RESPONDING TO ECD TOO

Fig. 7. Determination of two pesticides in a mixture, demonstrating the data processing.



REGISTER OF PESTICIDE RESIDUES OF 1 SAMPLE

NO	SAMPLE	NAME	PPM	RT	EXP.RT	REL.RT
CALCULATED FROM STANDARD MIXTURE I FOR P- COMPOUNDS						
4	SALAD	PT	.35	5.46	5.47	.311
4	SALAD	NT	1.00	17.61	17.61	1.000

CALCULATED FROM STANDARD MIXTURE II FOR P-COMPOUNDS

4	SALAD	PT	.09	5.46	5.46	.310
4	SALAD	AMIDITHION*	3.27	15.83	15.69	.891
4	SALAD	FENTHION	1.35	16.57	16.57	.941
4	SALAD	NT	1.00	17.61	17.61	1.000

THE DIFFERENCE BETWEEN THE DETECTORS AMOUNTS TO 88.0863 %
FOR AMIDITHION*

CALCULATED FROM STANDARD MIXTURE FOR N-COMPOUNDS

4	SALAD	PT	.96	5.46	5.46	.310
4	SALAD	DICHLOFLUA*	6.32	15.83	15.83	.899
4	SALAD	NT	1.00	17.61	17.61	1.000

THE DIFFERENCE BETWEEN THE DETECTORS AMOUNTS TO 24.9701 %
FOR DICHLOFLUA*

****

FENTHION IS IDENTIFIED ONLY WITH NPD IN SALAD
DICHLOFLUA* IS SUSPECTED IN SALAD

****

* BELONGS TO A CRITICAL PESTICIDE THAT INDICATES SIMILAR RETENTION TIME TO A COMPOUND OF ANOTHER STANDARD MIXTURE

** BELONGS TO A COMPOUND RESPONDING TO ECD TOO

Fig. 8. Pesticide screening in a real food sample.

with compounds in test mixture I. In Figs. 5 and 6 the chromatograms recorded with both detectors and the corresponding reports are shown.

The following example is selected to demonstrate how the system works. Two pesticides responding to both detectors were mixed with three internal standards. The chromatograms recorded in parallel are shown in Fig. 7. In addition to the internal standards, two peaks representing the two pesticides are found in both records. One of these peaks is recognized as fenitrothion on both channels, and the comparative calculation confirms the identity. The other peak is recognized by using the various calibration tables as either fensulfothion, chlorthiophos or binapacryl, because all three pesticides exhibit similar retention. Additionally, they all respond to both detectors, but the response factors are quite different, allowing the discrimination (see Fig. 7). A discrimination window has been set in the BASIC program, tolerating not more than a 30% difference in the quantitative results on both channels. This limit has proved to give reliable results in routine analysis for all critical pairs.

Finally we want to document a real sample from our routine work. In winter time, cabbage lettuce is cultivated in greenhouses where it is common practice to protect it with fungicides and insecticides. Many of these pesticides can be detected by the multiresidue analysis described here. In Fig. 8 the chromatograms of a cabbage lettuce sample are shown, together with the report of the data system. The fungicide dichlofluanid and the insecticide fenthion were identified and tentatively quantitated in the automated screening test and were later confirmed by on-column injection on the BP 10 column.

CONCLUSIONS

Automated GC on "bonded-phase" fused-silica columns with parallel detection of the effluent, split for ECD and NPD, is very suitable for pesticide multiresidue analysis of food samples. Applying the splitless injection technique, a detection in the lower ppb(10^9) range is obtained for the majority of pesticides as required to meet legal limits. For the screening of food samples for pesticide residues, dual-channel on-line data processing is a valuable aid to the analyst in selecting the samples suspected of contamination. The application of microprocessors, programmed according to the analyst's special needs, has been demonstrated to facilitate the decision making in the screening procedure. The final confirmatory test and the quantitation, however, must be carried out by the analyst manually by using appropriate test mixtures for each sample, composed individually on the basis of the screening results. It must be emphasized that the entire pesticide analysis can be performed with only one gas chromatograph and two capillary columns of different polarities, connected to the two selective detectors. The method described here has been successfully used with other capillary columns for more than 2 years in the routine analysis of food samples and is ready for the incorporation of additional compounds.

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