ELSEVIER

Journal of Chromatography A, 750 (1996) 369–390

JOURNAL OF CHROMATOGRAPHY A

Pesticide residue analysis in foodstuffs applying capillary gas chromatography with atomic emission detection State-of-the-art use of modified multimethod S19 of the Deutsche Forschungsgemeinschaft and automated large-volume injection with programmed-temperature vaporization and solvent venting

Hans-Jürgen Stan*, Manfred Linkerhägner

Technical University Berlin, Institute of Food Chemistry, Gustav-Meyer-Allee 25, D-13355 Berlin, Germany

Abstract

Atomic emission detection (AED) provides high element-specific detection of all compounds amenable to gas chromatography (GC). The heteroatoms nitrogen, chlorine, phosphorus, sulfur, bromine and fluorine, which are important elements in pesticide residue analysis, are of major interest. A main drawback of AED is its lower sensitivity with respect to other selective detection methods used in pesticide residue analysis such as electron-capture and nitrogen–phosphorus detection. This holds true especially for the important nitrogen trace. For this reason, more sensitive detection can be achieved by injection of larger volumes or higher concentrations of sample extracts, because matrix compounds were usually registered only in the carbon, hydrogen and oxygen traces. This paper focuses on recent developments from the authors' laboratory in order to demonstrate the feasibility of screening analyses with the identification of pesticide residues down to the 0.01 ppm concentration level in plant foodstuffs. This has been achieved by means of automated large volume injection with programmed-temperature vaporization and solvent venting as well as careful optimization of make-up and reactant gases with AED. Clean up follows the principle of multimethod S19 of the Deutsche Forschungsgemeinschaft in a reduced procedure. After elimination of lipids and waxes by gel permeation chromatography, extracts from 10 g of the food samples were concentrated to 200 μl, of which 12.5 μl were introduced into the GC–AED system. Two analyses were usually performed with the element traces of sulfur, phosphorus, nitrogen and carbon in the first run and chlorine and bromine in the second run. Fluorine and oxygen were not detected in any screening analyses. The method has proved to be of great value especially with "problem foodstuffs". The limits of detection were determined for 385 pesticides and are presented together with their retention data.

Keywords: Food analysis; Atomic emission detection; Detection, GC; Pesticides

1. Introduction

Pesticides always contain several heteroatoms in their molecules. Therefore, from the early days of pesticide residue analysis, selective detection methods were successfully applied in GC analysis. Electron-capture detection (ECD) made it possible to detect the chlorinated hydrocarbon pesticides in both food and later their ubiquitous occurrence in the environment. A few years later, nitrogen–phosphorus detection (NPD) was introduced first as alkali flame

*Corresponding author.

0021-9673/96/$15.00
PII S0021-9673(96)00616-4

ionization detection (AFID) which was able to detect nitrogen- and phosphorus- containing compounds. A number of other detection methods are in widespread use but they all are often not sufficiently selective, so that coextracted matrix compounds are also detected, complicating the interpretation of resulting chromatograms.

The frequency of heteroatoms is in the following order: N>Cl>S>P>F>Br. From 385 pesticides (including a few metabolites) 277 contain nitrogen, 181 chlorine, 146 sulfur, 100 phosphorus, 29 fluorine, 14 bromine, 3 iodine and one compound silicon as heteroatoms. From this large number, 4 active substances contain only nitrogen and 17 only chlorine as heteroatoms. Another 49 pesticides contain, besides nitrogen, only oxygen as a second heteroatom. The large number of polychlorinated biphenyl (PCB) congeners, other chlorinated hydrocarbons of industrial origin as well as the isomers of toxaphene also contain chlorine as their only indicative heteroatom. The majority of the pesticides, however, contain more than one heteroatom as can also be seen from Table 2 in this paper.

When analyzing for one element, all other elements must be transparent to the detector for this to be a truly element-specific detector. Atomic emission detection (AED) has proved to be highly selective for the recorded element and shows minimal cross selectivity. It actually has a selectivity of several thousand or more over carbon which is, of course, present in the bulk of coextracted matrix compounds. The first successful coupling of AED to gas chromatography (GC) was reported by two groups in 1965 [1,2]. The GC–AED system was introduced in 1989 by Hewlett-Packard as an analytical instrument, which is fully automated and uses a photodiode array spectrometer to allow the simultaneous detection of four elements [3,4]. A recent review of the principles and applications of contemporary methods of element selective chromatographic detection has been given by Uden [5].

The new detector has been successfully used in pesticide residue analysis of plant foodstuffs [6–10] and also in water [11–15]. The application of GC–AED to pesticide residue analysis and clean-up methods in water has recently been described in a monograph on pesticide analysis in water [16–19].

In this paper, the state-of-the-art of applying this technique to pesticide residue analysis in plant foodstuffs as well as our own experience in using GC–AED in routine analysis is reported.

2. Experimental

2.1. Gas chromatography

GC analyses were performed with an Hewlett-Packard (HP) Model 5890A Series II gas chromatograph equipped with an HP 7673A autosampler and HP 5921A atomic emission detector. The chromatograph was fitted with a 25 m×0.32 mm I.D. fused-silica capillary column coated with a 0.17 μm film of HP-1 (SE-30). As precolumn a 5 m×0.32 mm I.D. retention gap deactivated with phenylsilicone was used.

The column temperature was held at 50°C for 2 min after injection, programmed at 25°C/min to 150°C which was held for 2.5 min, then at 3°C to 205°C, and finally at 10°C/min to 250°C which was held for 10 min. Helium of 99.999% purity was used as carrier gas.

2.2. Programmed-temperature vaporization

PTV injection was performed with a KAS 3 inlet (Gerstel, Mühlheim, Germany). The KAS 3 inlet was equipped with a 92 mm×1.2 mm I.D. deactivated empty glass liner with baffles. 12.5 μl were injected by an autosampler, equipped with a 25 μl syringe. The injector starting temperature was 40°C. Column head pressure was adjusted to 6.2·104 Pa and flow-rate through the split vent to 40 ml/min. After 40 s, the split valve was closed and the liner flash heated at 12°C/s to 260°C, which was held for 1 min. The split valve was then opened and the liner further heated at 12°C/s to 300°C, which was held for 1 min.

2.3. Atomic emission detection

The transfer line to the detector and the detector cavity were operated at 240 and 300°C, respectively. The spectrometer was purged with nitrogen at 2 l/min and the window with helium at 30 ml/min. Helium at 30 ml/min was used as make-up gas. The reagent gases were hydrogen at $2.1 \cdot 10^5$ and oxygen at $1.4 \cdot 10^5$ Pa; for oxygen measurement, $3.5 \cdot 10^5$ 10%

CH_4 in N_2 was used. The cooling water temperature was 63°C. Data were processed with a HP AED-Chemstation 5895A.

2.4. Materials

All solvents were Pestanal products from Riedel-De Haën (Seelze, Germany) and all analytical standards were supplied by Promochem (Wesel, Germany).

2.5. Sample preparation—clean up with modified multimethod S19

Food samples were prepared using the S19 multimethod of the Deutsche Forschungsgemeinschaft (DFG) Pesticide Commission [10,20] but only 20 g of homogenized plant material were extracted with 40 ml acetone. Before the extraction began, 2 μg aldrin dissolved in toluene was added as surrogate standard (SSTD) representing a pesticide concentration of 0.1 ppm. The extract was saturated with sodium chloride and diluted with 25 ml dichloromethane, in order to separate excess water. The extract phase was cleaned up by gel permeation chromatography (GPC) on Bio-Beads S-X3 polystyrene gel, using a mixture of cyclohexane–ethyl acetate (1:1, v/v) as eluent. The eluates were evaporated to dryness and redissolved in 200 μl toluene, and transferred to autosampler vials and injected into the gas chromatograph. 12.5 μl of the extract was equivalent to 625 mg plant material.

A supplemental clean up and fractionation was carried out on silica minicolumns. Modifying the original method, the sample extract was separated into three fractions, namely fraction 1 with toluene, fraction 2 with toluene–acetone (80:20, v/v) and fraction 3 with acetone. To fractions 2 and 3, chlorthion was added as internal standard (I.S.) to give a concentration of 0.2 ppm.

3. Results and discussion

3.1. Optimization of the detection sensitivity in the various element traces

The detection sensitivity in the various element traces is dependent on the gas flow in the cavity. With all elements, helium make-up gas is applied. Depending on the element, the addition of reactant gases is necessary. Starting with the recommendations of the manufacturer, the optimization was carried out by varying the individual parameters in preliminary experiments followed by fine tuning as will be demonstrated here for one simple case, the element trace of chlorine.

Although the detector response in an element trace theoretically should not depend on the type of molecule in which the atom is bound, mixtures of pesticides were analyzed in every optimization procedure. These mixtures were composed of pesticides containing a different number of atoms of the element together with other heteroatoms and different bonds such as aliphatic or aromatic in the case of chlorine. The mixture used for optimization of the chlorine trace is given in Fig. 1.

3.1.1. Dependence of chlorine-selective detection on make-up gas flow

The detection of chlorine and bromine needs the addition of oxygen gas to the make-up gas. In preliminary experiments a pressure of 25 p.s.i. (1 p.s.i.=6894.76 Pa) for oxygen was found to give good results. The flow of the make-up gas was varied stepwise and each measurement was repeated five times. All results presented in the graphics in Fig. 1 are the mean values of 5 injections

As can be seen from Fig. 1, there is, as expected, an increase of the peak area with the reduction of the make-up gas flow. Although a further reduction of make-up gas results in a further increase of peak areas this is accompanied by peak broadening. Therefore, the optimum of the make-up gas flow was considered to be 40 ml/min. As can be drawn from Fig. 1, the response reflects the number of chlorines in the molecule. Interestingly, the two stereoisomers of HCH show different responses, with β-HCH exhibiting in all experiments a greater similarity in its response to pentachlorobenzene than to α-HCH which was found to be the compound with the highest response.

3.1.2. Dependence of chlorine-selective detection on oxygen gas flow

The fine tuning of the chlorine-selective detection was carried out by changing the oxygen gas pressure with a constant make-up gas flow of 40 ml/min. The

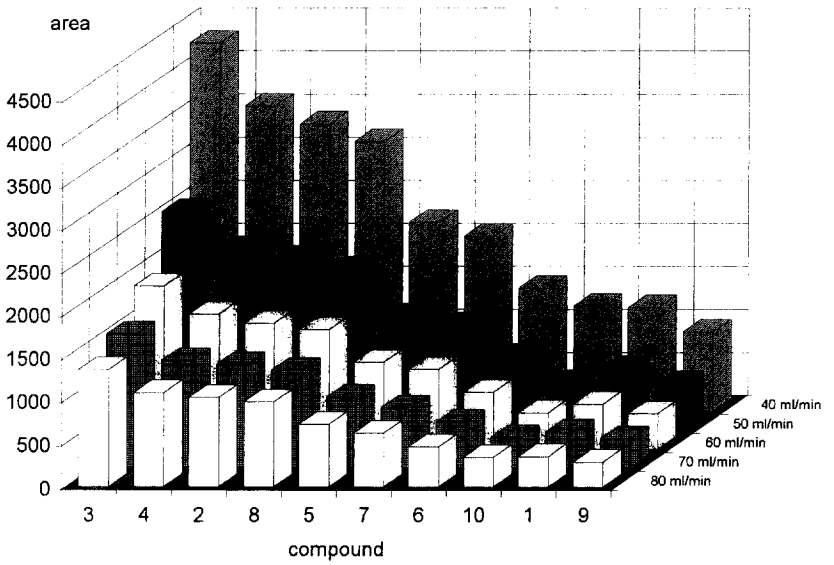

Fig. 1. Dependence of chlorine selective detection on make-up gas flow. Make-up gas: variable; reactant gas O_2: 25 p.s.i.. Test mixture: 1=dichlorvos; 2=pentachlorobenzene; 3=α-HCH; 4=β-HCH; 5=triallate; 6=fenclorphos; 7=dichlofluanid; 8=aldrin; 9=bromophos-methyl; 10=penconazole (20 ng of each pesticide injected).

results are given in the graphical plot in Fig. 2. A pressure of only 10 ml/min was found to give the highest response with all test substances. The relative responses of the test compounds show the same ranking as with the make-up gas flow variation within the reproducibility of the measurements.

3.1.3. Discussion of the reactant gas optimization

As a result of our extensive optimization procedure, we found the parameters compiled in Table 1 give the highest detection sensitivity with our instrument. It must, however, be noted that in discussions with other groups working with GC–AED it seems

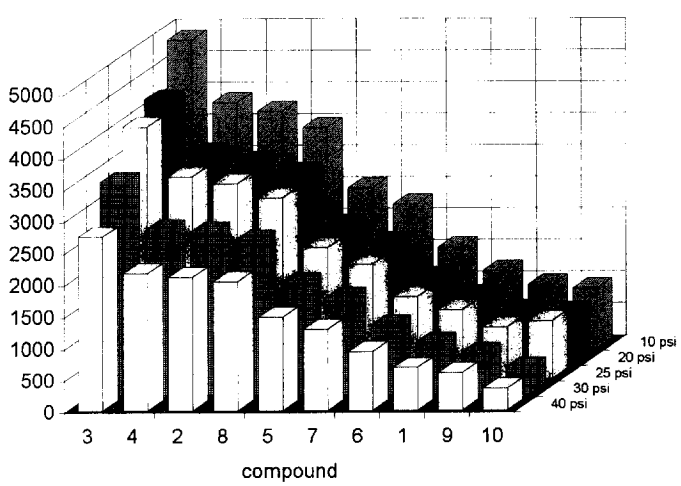

Fig. 2. Dependence of chlorine selective detection on oxygen gas flow. Reactant gas O_2: variable; make-up gas: 40 ml/min. Test mixture as in Fig. 1.

that the detection sensitivity finally achieved is also dependent on the individual instrument.

A make-up gas flow of 40 ml/min helium was found best for C, N, S, Cl, Br and O with respect to high response and acceptable peak form, whereas phosphorus needs a much higher flow of 180 ml/min and fluorine at least 60 ml/min. These results are in agreement with those of Quimby and Sullivan [3], they worked with chlorine with only 10 ml/min make-up gas flow. In our hands, the make-up gas flow of 20 ml/min was a critical lower limit due to a rapid decrease of the response below this flow. Therefore, for a series of analyses, such as in routine pesticide residue analysis, a make-up gas flow of 40 ml/min was chosen to guarantee unattended automated sample analysis. Lowering the oxygen pressure to 10 p.s.i. gives increased detection sensitivity for most elements. Since oxygen protects the cavity from carbonization, a minimum pressure of 20 p.s.i. was set as our limit in order to obtain longer operational periods with constant detection sensitivity. A hydrogen pressure of 30 p.s.i. was found to be optimum for all element traces, with better response values compared to the recommended 70 p.s.i. (see Table 1).

3.2. Determination of the limit of detection with GC–AED

Analytical results are always approaches to the real concentration in a sample. They are particularly prone to analytical errors close to the limit of detection (LOD). There are many methods for the definition of this most critical parameter of any analytical procedure. They all have in common the factor that the signal (GC peak) must have undoubtedly risen above the so-called chemical or electronic noise. The definition of a significant peak coming out of the noise is a wide field of statistical theory and dispute [21–23].

However, a definition or consent is necessary when analytical results at trace levels are to be evaluated. The same holds true when different detection principles need to be compared with respect to their applicability to pesticide residue analysis in food and also water samples.

In order to illustrate the general uncertainty in this field, a few of our many results that have been obtained with three different methods for the estimation of LODs are presented.

All instructions demand analysis of blank samples that are completely processed through all analytical steps, with background signal measurement with the detection system at the highest sensitivity level. With chromatographic detectors, the noise is recorded within a time interval of 2 min around the retention time of the observed peak. The noise is recorded as at least 20 small peaks with their peak heights.

In the present study, the application of GC–AED in pesticide residue analysis of 400 pesticides after clean-up using a multimethod applicable to a great variety of plant foodstuffs was investigated. The

Table 1
Optimum parameter settings for reactant gases and "make-up" gas flow

Element/ wavelength (nm)	Make-up gas He (ml/min)	O_2	Reactant gases (p.s.i.)[a] H_2	10% CH_4 in N_2
C 193	40	20	30	
N 174	40	20	30	
S 181	40	20	30	
P 178	180		30	
Cl 479	40	20		
Br 478	40	20		
F 690	60		30	
O 777	40		30	30

[a] Adjusted at the pressure regulator.

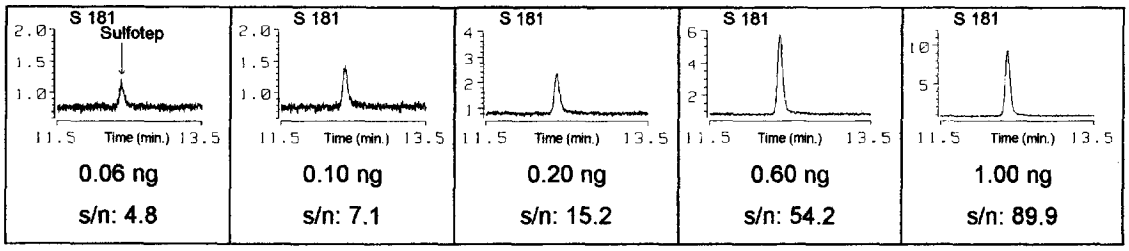

Fig. 3. Detection of sulfotep in the sulfur trace—amount injected as indicated.

detection of the pesticides was carried out by means of seven element-selective traces. It was clear that a more practical approach than that described above was needed to obtain the experimental data for a reliable evaluation.

In the first experiments, AED proved its extremely high element selectivity. The element traces of the most interesting hetero atoms N, Cl, S, P, Br and F were found actually free or almost free of peaks from co-eluted matrix. Therefore, the element trace recordings of injections of blank samples, pure solvent or a run without any injection were not different. Only by means of the simultaneously recorded carbon trace were these analyses distinguishable. the "problem foodstuffs" onion, leek and garlic that contain many volatile sulfur compounds were of course an exception.

A great amount of raw data were used for the calculation of the LODs with three different mathematical methods [24–26]. The mathematical treatment resulted in theoretical LODs that varied with the three methods but more importantly they were found to be remarkably different from those actually observed in pesticide residue analysis. Therefore, a more practical approach has been applied which will be demonstrated with examples, namely the two pesticides sulfotep in the sulfur trace and lindane in the chlorine trace. The mathematical treatment with the various methods and the resulting LODs including a detailed discussion of the determination of LODs is presented elsewhere [27,28].

In the chromatograms of Figs. 3 and 4 the peaks are shown with their signal to noise ratios (S/N). Injections of 60 pg sulfotep and 126 pg lindane are clearly detectable. The graphical plots show straight linear functions of the detector response and compound concentration. From Figs. 3 and 4 it can be deduced that the LOD in the sulfur trace for sulfotep is about 50 pg and the LOD for lindane in the chlorine trace is about 120 pg. In this way LODs have been determined in all relevant element traces. The results are presented in Table 2.

3.3. Linear dynamic range (LDR)

Although the LDR is of great importance for the evaluation of an analytical method, there is, to our knowledge, no general consent about its definition. In particular it seems unclear, how large a range of variation of signal values is acceptable in considering the function of signal and concentration as linear. The coefficients of correlation are of little help in the evaluation. The confidence interval was proposed for

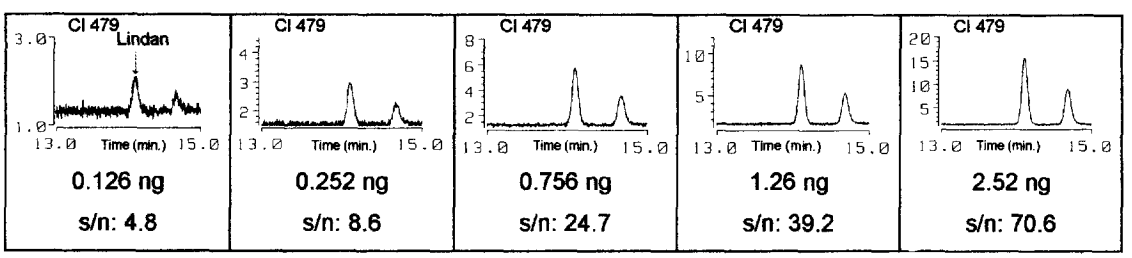

Fig. 4. Detection of lindane in the chlorine trace—amount injected as indicated.

Table 2
Limit of detection of 385 pesticides and metabolites using modified multimethod S19 and GC–ACED

Pesticide	Formula	Limit (ppb)							t_R (min)[a]
		N	P	O	S	F	Cl	Br	
Acephate	$C_4H_{10}NO_3PS$	20	12	40	1				9.51
Acetochlor	$C_{14}H_{20}ClNO_2$	40		12			2		18.73
Alachlor	$C_{14}H_{20}ClNO_2$	40		12			1		19.24
Aldrin	$C_{12}H_8C_{16}$						0.4		20.78
Allethrin	$C_{19}H_{26}O_3$			20					23.25
Ametryne	$C_9H_{17}N_5S$	12			1				19.50
Amidithion	$C_7H_{16}NO_4PS_2$	40	12	20	0.4				9.51
Aminocarb	$C_{11}H_{16}N_2O_2$	40		20					18.73
Amitraz	$C_{19}H_{23}N_3$	20							33.91
Ancymidol	$C_{15}H_{16}N_2O_2$	20		20					27.96
Anilazine	$C_9H_5Cl_3N_4$	60					12		23.56
Anthraquinon	$C_{14}H_8O_2$			20					21.05
Aramite	$C_{15}H_{23}ClO_4S$			20	1		12		27.81
Atratone	$C_9H_{17}N_5O$	12		40					14.76
Atrazine	$C_8H_{14}ClN_5$	4					1		15.26
Atrazine desethyl	$C_6H_{10}ClN_5$	12					4		13.62
Atrazine desethyldesisopropyl	$C_3H_4ClN_5$	12					4		11.66
Atrazine desisopropyl	$C_5H_8ClN_5$	12					4		13.02
Azaconazole	$C_{12}H_{11}Cl_2N_3O_2$	20		20			2		27.35
Azamethiphos	$C_9H_{10}ClN_2O_5PS$	60	12	20	4		20		27.15
Azinphos ethyl	$C_{12}H_{16}N_3O_3PS_2$	20	12	40	1				34.66
Azinphos methyl	$C_{10}H_{12}N_3O_3PS_2$	20	12	40	1				33.11
Aziprotryne	$C_7H_{11}N_7S$	12			1				16.78
Azobenzene	$C_{12}H_{10}N_2$	4							12.48
Barbane	$C_{11}H_9Cl_2NO_2$	20		20			4		26.78
Benalaxyl	$C_{20}H_{23}NO_3$	20		12					29.64
Benazolin ethyl	$C_{11}H_{10}ClNO_3S$	40		12	0.4		2		23.38
Benazolin methyl	$C_{10}H_8ClNO_3S$	40		12	0.4		2		21.76
Bendiocarb	$C_{11}H_{13}NO_4$	20		4					13.52
Benfluralin	$C_{13}H_{16}F_3N_3O_4$	12		4		4			13.61
Benodanil	$C_{13}H_{10}INO$	60		40				J:60	29.01
Bentazone	$C_{10}H_{12}N_2O_3S$	12		20	0.4				22.62
Benzoylprop ethyl	$C_{18}H_{17}Cl_2NO_3$	60		12			1		31.31
Bifenox	$C_{14}H_9Cl_2NO_5$	40		20			2		32.40
Bifenthrin	$C_{23}H_{22}ClF_3O_2$			20		4	4		31.93
Binapacryl	$C_{15}H_{18}N_2O_6$	12		4					28.16
Bitertanol I	$C_{20}H_{23}N_3O_2$	20		20					35.75
Bitertanol II	$C_{20}H_{23}N_3O_2$	60		40					36.00
Bromacil	$C_9H_{13}BrN_2O_2$	12		20				4	20.91
Bromocyclen	$C_8H_5BrCl_6$						0.4	2	17.29
Bromophos	$C_8H_8BrCl_2O_3PS$		4	20	1		2	2	22.46
Bromophos ethyl	$C_{10}H_{12}BrCl_2O_3PS$		4	20	1		2	2	25.00
Bromoxynil	$C_7H_3Br_2NO$	40		40				4	13.58
Bromopropylate	$C_{17}H_{16}Br_2O_3$			12				2	31.70
Bromuconazole	$C_{13}H_{12}BrCl_2N_3O$	20		40			2	2	32.42
Bupirimate	$C_{13}H_{24}N_4O_3S$	20		20	2				27.60
Butachlor	$C_{17}H_{26}ClNO_2$	40		12			1		25.86
Butralin	$C_{14}H_{21}N_3O_4$	12		4					22.63

(Continued on p. 376)

Table 2 (*continued*)

Pesticide	Formula	Limit (ppb)							t_R (min)[a]
		N	P	O	S	F	Cl	Br	
Butylate	$C_{11}H_{23}NOS$	12		12	0.4				9.21
Captafol	$C_{10}H_9Cl_4NO_2S$	40		20	2		1		30.51
Captan	$C_9H_8Cl_3NO_2S$	40		20	1		1		23.68
Carbaryl	$C_{12}H_{11}NO_2$	20		12					19.22
Carbetamide	$C_{12}H_{16}N_2O_3$	20		12					22.16
Carbofuran	$C_{12}H_{15}NO_3$	20		4					15.10
Carbophenothion	$C_{11}H_{16}ClO_2PS_3$		2	40	0.4		2		29.52
Carbosulfan	$C_{20}H_{32}N_2O_3S$	20		4	0.4				31.68
Carboxin	$C_{12}H_{13}NO_2S$	40		20	4				27.20
Chinomethionat	$C_{10}H_6N_2OS_2$	40		40	0.4				28.51
Chlorbenside	$C_{13}H_{10}Cl_2S$				0.4		1		24.33
Chlorobenzilate	$C_{16}H_{14}Cl_2O_3$			20			1		28.23
Chlorbromuron	$C_9H_{10}BrClN_2O_2$	20		20			20	12	23.31
Chlorbufam	$C_{11}H_{10}ClNO_2$	12		12			2		15.15
Chlordecon	$C_{10}Cl_{10}O$			40			0.4		28.88
Chlordimeform	$C_{10}H_{13}ClN_2$	20					12		18.60
Chlorfenethol	$C_{14}H_{12}Cl_2O$			20	1				23.60
Chlorfenson	$C_{12}H_8Cl_2O_3S$			20	1		1		26.00
Chlorfenvinphos	$C_{12}H_{14}Cl_3O_4P$		4	20			1		24.00
Chloridazon	$C_{10}H_8ClN_3O$	12		40			12		30.53
Chlormephos	$C_5H_{12}ClO_2PS_2$		1	12	0.4		1		9.37
Chloroneb	$C_8H_8Cl_2O_2$			12			1		10.33
Chlorpropham	$C_{10}H_{12}ClNO_2$	20		12			1		12.96
Chloropropylate	$C_{17}H_{16}Cl_2O_3$			12			2		28.25
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	12	1	12	0.4		1		21.55
Chlorpyrifos methyl	$C_7H_7Cl_3NO_3PS$	12	1	12	0.4		1		18.81
Chlorthalonil	$C_8Cl_4N_2$	20					1		17.03
Chlorthiamid	$C_7H_5Cl_2NS$	12			1		2		18.43
Chlorthion	$C_8H_9ClNO_5PS$	20	2	20	0.4		2		22.12
Chlorthiophos I	$C_{11}H_{15}Cl_2O_3PS_2$		4	40	0.4		2		28.13
Chlorthiophos II	$C_{11}H_{15}Cl_2O_3PS_2$		4	40	0.4		2		28.46
Chlorthiophos III	$C_{11}H_{15}Cl_2O_3PS_2$		4	40	0.4		2		28.96
Chlozolinate	$C_{13}H_{11}C_{12}NO_5$	20		12			4		23.81
Coumaphos	$C_{14}H_{16}ClO_5PS$		12	20	2		4		36.73
Crotoxyphos	$C_{14}H_{19}O_6P$		4	12					24.67
Crufomate	$C_{12}H_{19}ClNO_3P$	60	20	40			12		22.32
Cyanazine	$C_9H_{13}ClN_6$	20					4		21.94
Cyanofenphos	$C_{15}H_{14}NO_2PS$	20	4	40	1				29.70
Cyanophos	$C_9H_{10}NO_3PS$	20	12	12	0.4				15.89
Cycloate	$C_{11}H_{21}NOS$	20		12	0.4				12.60
Cycluron	$C_{11}H_{22}N_2O$	12		20					15.74
Cymoxanil	$C_7H_{10}N_4O_3$	20		12					12.29
Cypermethrin I	$C_{22}H_{19}Cl_2NO_3$	40		20			4		39.25
Cypermethrin II	$C_{22}H_{19}Cl_2NO_3$	40		20			4		39.69
Cypermethrin III	$C_{22}H_{19}Cl_2NO_3$	40		20			4		39.65
Cypermethrin IV	$C_{22}H_{19}C_{12}NO_3$	40		20			4		40.16
Cyprofuram	$C_{14}H_{14}ClNO_3$	12		12			4		28.61
Cyromazine	$C_6H_{10}N_6$	12							15.51

Table 2 (*continued*)

Pesticide	Formula	Limit (ppb)							t_R (min)[a]
		N	P	O	S	F	Cl	Br	
2,4-D Isobutyl	$C_{12}H_{14}Cl_2O_3$			12			1		17.50
Dazomet	$C_5H_{10}N_2S_2$	12			0.4				14.59
o,p'-DDD	$C_{14}H_{10}Cl_4$						0.4		27.13
p,p'-DDD	$C_{14}H_{10}C_{14}$						0.4		28.59
o,p'-DDE	$C_{14}H_8Cl_4$						0.4		24.98
p,p'-DDE	$C_{14}H_8Cl_4$						0.4		26.62
o,p'-DDT	$C_{14}H_9Cl_5$						0.4		28.60
p,p'-DDT	$C_{14}H_9Cl_5$						0.4		29.86
Deltamethrin	$C_{22}H_{19}Br_2NO_3$	40		12				2	48.01
Demephion	$C_5H_{13}O_3PS_2$		12	20	1				10.83
Demeton	$C_8H_{19}O_3PS_2$		12	40	2				14.60
Demeton S methyl	$C_6H_{15}O_3PS_2$		2	12	0.4				12.33
Demeton S methylsulfon	$C_6H_{15}O_5PS_2$		2	12	0.4				20.18
Desmetryn	$C_8H_{15}N_5S$	12			1				18.33
Dialifos	$C_{14}H_{17}ClNO_4PS_2$	40	12	40	1		4		34.93
Diallate I	$C_{10}H_{17}Cl_2NOS$	20		12	0.4		1		13.79
Diallate II	$C_{10}H_{17}Cl_2NOS$	60		40	2		4		14.16
Diazinon	$C_{12}H_{21}N_2O_3PS$	40	2	20	2				16.56
Dicapthon	$C_8H_9ClNO_5PS$	40	4	20	0.4		1		21.81
Dichlobenil	$C_7H_3Cl_2N$	20					1		8.22
Dichlofenthion	$C_{10}H_{13}Cl_2O_3PS$		12	12	0.4		1		18.35
Dichlofluanid	$C_9H_{11}Cl_2FN_2O_2S_2$	12		12	0.4	12	1		20.68
Dichlone	$C_{10}H_4Cl_2O_2$			20			4		16.49
4,4-Dichlorodibenzophenone	$C_{13}H_8Cl_2O$			40			1		21.61
Dichlorvos	$C_4H_7Cl_2O_4P$		1	12			1		7.22
Diclobutrazol	$C_{15}H_{19}Cl_2N_3O$	12		40			2		27.22
Dicloran	$C_6H_4Cl_2N_2O_2$	20		20			1		14.63
Dicofol	$C_{14}H_9Cl_5O$			40			1		31.93
Dicrotophos	$C_8H_{16}NO_5P$	20	4	12					13.43
Dieldrin	$C_{12}H_8Cl_6O$			40			0.4		26.53
Diflufenican	$C_{19}H_{11}F_5N_2O_2$	20		20		2			13.42
Dimefox	$C_4H_{12}FN_2OP$	20	1	20		12			6.86
Dimetachlor	$C_{13}H_{18}ClNO_2$	20		12			4		18.38
Dimethametryn	$C_{11}H_{21}N_5S$	40			2				23.53
Dimethipin	$C_6H_{10}O_4S_2$			4	0.4				15.26
Dimethoate	$C_5H_{12}NO_3PS_2$	40	2	20	0.4				14.78
Dimethylaminosulfanilide	$C_8H_{12}N_2O_2S$	20		12	2				15.77
Dimethylaminosulfotouidide	$C_9H_{14}N_2O_2S$	20		12	2				13.36
Dinobuton	$C_{14}H_{18}N_2O_7$	12		4					24.42
Dinocap I	$C_{18}H_{24}N_2O_6$	60		20					30.86
Dinocap II	$C_{18}H_{24}N_2O_6$	60		20					31.28
Dinocap III	$C_{18}H_{24}N_2O_6$	200		60					31.73
Dinocap IV	$C_{18}H_{24}N_2O_6$	60		20					32.15
Dinocap V	$C_{18}H_{24}N_2O_6$	200		60					33.09
Dinoseb	$C_{10}H_{12}N_2O_5$	20		4					16.71
Dinoseb acetate	$C_{12}H_{14}N_2O_6$	20		4					19.80
Dinoterb	$C_{10}H_{12}N_2O_5$	20		4					16.16
Dinoterb acetate	$C_{12}H_{14}N_2O_6$	20		4					20.18

(*Continued on p. 378*)

Table 2 (*continued*)

Pesticide	Formula	Limit (ppb)							t_R (min)[a]
		N	P	O	S	F	Cl	Br	
Dioxacarb	$C_{11}H_{13}NO_5$	40		12					18.32
Dioxathion	$C_{12}H_{26}O_6P_2S_4$		1	12	0.4				15.58
Diphenamid	$C_{16}H_{17}NO$	20		12					22.59
Diphenylamine	$C_{12}H_{11}N$	20							12.32
Dipropetryn	$C_{11}H_{21}N_5S$	12			1				21.15
Disulfoton	$C_8H_{19}O_2PS_3$		12	40	0.4				16.65
Ditalimfos	$C_{12}H_{14}NO_4PS$	20	4	12	0.4				25.84
DNOC	$C_7H_6N_2O_5$	4		4					12.26
Drazoxolon	$C_{10}H_8ClN_3O_2$	40		20			4		22.31
Edifenphos	$C_{14}H_{15}O_2PS_2$		4	20	0.4				29.72
α-Endosulfan	$C_9H_6Cl_6O_3S$			12	1		0.4		25.08
β-Endosulfan	$C_9H_6Cl_6O_3S$			12	1		0.4		27.95
Endosulfan-sulfate	$C_9H_6Cl_6O_4S$			12	1		0.4		29.62
Endrin	$C_{12}H_8Cl_6O$			20			0.4		27.53
EPN	$C_{14}H_{14}NO_4PS$	40	4	20	1				31.72
Epoxiconazole	$C_{17}H_{13}ClFN_3O$	4		20		12	2		31.06
EPTC	$C_9H_{19}NOS$	12		12	0.4				8.25
Etaconazole I	$C_{14}H_{15}Cl_2N_3O_2$	20		20			2		28.50
Etaconazole II	$C_{14}H_{15}Cl_2N_3O_2$	20		20			2		28.66
Ethalfluralin	$C_{13}H_{14}F_3N_3O_4$	4		4		4			13.20
Ethiolate	$C_7H_{15}NOS$	12		12	0.4				6.95
Ethion	$C_9H_{22}O_4P_2S_4$		0.4	20	0.4				28.87
Ethofumesate	$C_{13}H_{18}O_5S$			4	0.4				20.64
Ethoprophos	$C_8H_{19}O_2PS_2$		1	20	0.4				12.59
Etridiazole	$C_5H_5Cl_3N_2OS$	12		12	0.4		0.4		9.56
Etrimfos	$C_{10}H_{17}N_2O_4PS$	12	4	12	1				17.31
Fenamiphos	$C_{13}H_{22}NO_3PS$	60	12	20	1				26.35
Fenarimol	$C_{17}H_{12}Cl_2N_2O$	60		40			4		34.26
Fenazaflor	$C_{15}H_7Cl_2F_3N_2O_2$	20		12		4	1		29.15
Fenchlorphos	$C_8H_8Cl_3O_3PS$		4	20	0.4		1		19.58
Fenfuram	$C_{12}H_{11}NO_2$	20		12					16.89
Fenitrothion	$C_9H_{12}NO_5PS$	40	2	12	0.4				20.41
Fenobucarb	$C_{12}H_{17}NO_2$	20		12					12.12
Fenoxycarb	$C_{17}H_{19}NO_4$	20		4					31.90
Fenpropathrin	$C_{20}H_{23}NO_3$	12		12					32.15
Fenpropimorph	$C_{20}H_{33}NO$	20		40					21.61
Fenson	$C_{12}H_9ClO_3S$			12	1		4		22.10
Fensulfothion	$C_{11}H_{17}O_4PS_2$		4	12	0.4				28.46
Fenthion	$C_{10}H_{15}O_3PS_2$		2	40	0.4				21.49
Fenuron	$C_9H_{12}N_2O$	40		40					12.64
Fenvalerate I	$C_{25}H_{22}ClNO_3$	40		12			4		43.23
Fenvalerate II	$C_{25}H_{22}ClNO_3$	40		12			4		44.38
Flamprop isopropyl	$C_{19}H_{19}ClFNO_3$	20		20		20	12		28.65
Flauzifop, *p*-butyl	$C_{19}H_{20}F_3NO_4$	20		12		12			28.17
Flubenzimine	$C_{17}H_{10}F_6N_4S$	20			2	12			27.12
Fluchloralin	$C_{12}H_{13}ClF_3N_3O_4$	12		4		12	4		16.74
Flumetralin	$C_{16}H_{12}ClF_4N_3O_4$	12		4		12	4		25.91
Fluometuron	$C_{10}H_{11}F_3N_2O$	20		20		12			12.70

Table 2 (*continued*)

Pesticide	Formula	Limit (ppb)							t_R (min)[a]
		N	P	O	S	F	Cl	Br	
Fluorodifen	$C_{13}H_7F_3N_2O_5$	12		12		4			26.48
Fluotrimazol	$C_{22}H_{16}F_3N_3$	4				4			31.02
Flurenol butyl	$C_{18}H_{18}O_3$			12					24.73
Fluridon	$C_{19}H_{14}F_3NO$	60		40		20			42.49
Flurochloridon	$C_{12}H_{10}Cl_2F_3NO$	20		20		12	2		22.44
Fluroxypr meptyl	$C_{15}H_{21}Cl_2FN_2O_3$	12		12		20	1		30.61
Flusilazol	$C_{16}H_{15}F_2N_3Si$	12				20		Si: 4	27.41
Flutriafol	$C_{16}H_{13}F_2N_3O$	20		20		20			25.82
Fluvalinate I	$C_{26}H_{22}ClF_3N_2O_3$	40		20		12	12		44.63
Fluvalinate II	$C_{26}H_{22}ClF_3N_2O_3$	40		20		12	12		45.10
Folpet	$C_9H_4Cl_3NO_2S$	20		20	0.4				24.12
Fonofos	$C_{10}H_{15}OPS_2$		4	40	0.4				16.05
Formothion	$C_6H_{12}NO_4PS_2$	60	4	20	0.4				17.80
Fuberidazol	$C_{11}H_8N_2O$	12		20					18.47
Furalaxyl	$C_{17}H_{19}NO_4$	20		12					24.41
Furathiocarb	$C_{18}H_{26}N_2O_5S$	40		20	4				32.94
Furmecyclox	$C_{14}H_{21}NO_3$	12		12					17.84
α-HCH	$C_6H_6Cl_6$						0.4		13.96
β-HCH	$C_6H_6Cl_6$						0.4		15.36
δ-HCH	$C_6H_6Cl_6$						0.4		16.82
γ-HCH	$C_6H_6Cl_6$						0.4		15.49
Heptachlor	$C_{10}H_5Cl_7$						0.4		19.00
cis-Heptachlorepoxide	$C_{10}H_5Cl_7O$						0.4		23.21
trans-Heptacchlorepoxide	$C_{10}H_5Cl_7O$			20			0.4		23.35
Heptenophos	$C_9H_{12}ClO_4P$		1	12			1		11.47
Hexabrombenzene	C_6Br_6							0.4	31.51
Hexachlorbenzene	C_6Cl_6						0.4		14.41
Hexaconazole	$C_{14}H_{17}Cl_2N_3O$	20		20			2		26.19
Hexazinon	$C_{12}H_{20}N_4O_2$	4		12					30.41
Imazlil	$C_{14}H_{14}Cl_2N_2O$	20		40			4		26.54
Iodofenphos	$C_8H_8Cl_2IO_3PS$		4		2		2	J:12	26.25
Ioxynil	$C_7H_3I_2NO$	20		40				J:4	20.18
Iprodion	$C_{13}H_{13}Cl_2N_3O_3$	20		20			2		31.46
Isazofos	$C_9H_{17}ClN_3O_3PS$	40	4	20	0.4		2		17.21
Isocarbamid	$C_8H_{15}N_3O_2$	4		12					15.73
Isofenphos	$C_{15}H_{24}NO_4PS$	60	4	20	1				24.00
Isomethiozin	$C_{12}H_{20}N_4OS$	12		20	1				21.72
Isoprocarb	$C_{11}H_{15}NO_2$	12		12					10.97
Isopropalin	$C_{15}H_{23}N_3O_4$	12		4					23.17
Isoxaben	$C_{18}H_{24}N_2O_4$	20		40					35.01
3,4,5-Landrin	$C_{11}H_{15}NO_2$	20		12					13.15
Lenacil	$C_{13}H_{18}N_2O_2$	20		40					29.95
Leptophos	$C_{13}H_{10}BrCl_2O_2PS$		20	12	4		2	2	33.13
Linuron	$C_9H_{10}Cl_2N_2O_2$	20		20			1		20.59
Malaoxon	$C_{10}H_{19}O_7PS$		4	12	1				19.13
Malathion	$C_{10}H_{19}O_6PS_2$		2	4	0.4				21.09
Mecarbam	$C_{10}H_{20}NO_5PS_2$	20	12	12	0.4				24.14
Mefluidide	$C_{11}H_{13}F_3N_2O_3S$	20		20	1	2			23.63

(*Continued on p. 380*)

Table 2 (*continued*)

Pesticide	Formula	Limit (ppb)							t_R (min)[a]
		N	P	O	S	F	Cl	Br	
Merphos I	$C_{12}H_{27}PS_3$		12		1				23.55
Merphos II	$C_{12}H_{27}PS_3$		12		2				26.80
Merphos III	$C_{12}H_{27}PS_3$		60		20				28.88
Metalaxyl	$C_{15}H_{21}NO_4$	20		12					19.66
Metamitron	$C_{10}H_{10}N_4O$	12		20					27.39
Metazachlor	$C_{14}H_{16}ClN_3O$	4		20			1		23.22
Methacriphos	$C_7H_{13}O_5PS$		2	12	0.4				10.22
Methamidophos	$C_2H_8NO_2PS$	20	1	12	0.4				7.18
Methazole	$C_9H_6Cl_2N_2O_3$	60		40			12		20.93
Methfuroxam	$C_{14}H_{15}NO_2$	20		12					21.92
Methidathion	$C_6H_{11}N_2O_4PS_3$	20	4	12	2				24.79
Methiocarb	$C_{11}H_{15}NO_2S$	20		12	2				20.46
Methoprotryne	$C_{11}H_{21}N_5OS$	12		20	0.4				27.08
Methoxychlor	$C_{16}H_{15}Cl_3O_2$			12			0.4		31.97
Metobromuron	$C_9H_{11}BrN_2O_2$	12		20				2	17.73
Metolachlor	$C_{15}H_{22}ClNO_2$	40		12			2		21.22
Metribuzin	$C_8H_{14}N_4OS$	4		20	0.4				18.58
Mevinphos	$C_7H_{13}O_6P$		2	12					9.15
Mirex	$C_{10}Cl_2$						0.4		33.27
Molinate	$C_9H_{17}NOS$	20		12	0.4				10.82
Monalide	$C_{11}H_{18}ClNO$	20		40			2		17.69
Monocrotophos	$C_7H_{14}NO_5P$	20	12	12					13.73
Monolinuron	$C_9H_{11}ClN_2O_2$	12		12			1		15.19
Myclobutanil	$C_{15}H_{17}ClN_4$	20					12		27.25
Naled	$C_4H_7Br_2Cl_2O_4P$		2	12			2	1	13.06
Napropamide	$C_{17}H_{21}NO_2$	40		20					26.16
Naptalam	$C_{18}H_{13}NO_3$	40		20					34.00
Nicotine	$C_{10}H_{14}N_2$	4							8.31
Nitralin	$C_{13}H_{19}N_3O_6S$	20		12	1				31.16
Nitrapyrin	$C_6H_3Cl_4N$	20					0.4		9.55
Nitrofen	$C_{12}H_7Cl_2NO_3$	12		12			2		27.69
Nitrothal isopropyl	$C_{14}H_{17}NO_6$	40		12					22.25
Norflurazon	$C_{12}H_9ClF_3N_3O$	12		20		4	2		29.95
Nuarimol	$C_{17}H_{12}ClFN_2O$	60		40		20	4		30.35
Omethoate	$C_5H_{12}NO_4PS$	40	12	20	1				11.84
Oryzalin	$C_{12}H_{18}N_4O_6S$	20		12	4				35.96
Oxabetrinil	$C_{12}H_{12}N_2O_3$	4		12					17.49
Oxadiazon	$C_{15}H_{18}Cl_2N_2O_3$	12		12			2		27.26
Oxadixyl	$C_{14}H_{18}N_2O_4$	40		20					28.87
Oxycarboxin	$C_{12}H_{13}NO_4S$	20		12	4				30.89
Oxydemeton methyl	$C_6H_{15}O_4PS_2$		2	12	1				19.71
Paclobutrazol	$C_{15}H_{20}ClN_3O$	20		40			4		25.07
Paraoxon	$C_{10}H_{14}NO_6P$	20	4	12					19.67
Paraoxon methyl	$C_8H_{10}NO_6P$	20	4	12					16.74
Parathion	$C_{10}H_{14}NO_5PS$	20	4	12	0.4				21.67
Parathion metyl	$C_8H_{10}NO_5PS$	20	4	12	0.4				18.88
Pebulate	$C_{10}H_{21}NOS$	20		12	0.4				9.62
Penconazole	$C_{13}H_{15}Cl_2N_3$	20					4		23.51

Table 2 (*continued*)

Pesticide	Formula	Limit (ppb)							t_R (min)[a]
		N	P	O	S	F	Cl	Br	
Pendimethalin	$C_{13}H_{19}N_3O_4$	20		12					23.41
Pentachlorobenzene	C_6HCl_5						0.4		10.52
Pentachlorophenol	C_6HCl_5O			40			1		15.44
Pentanochlor	$C_{13}H_{18}ClNO$	60		40			4		20.67
Permethrin I	$C_{21}H_{20}Cl_2O_3$			20			4		36.01
Permethrin II	$C_{21}H_{20}Cl_2O_3$			12			2		36.43
Perthane	$C_{18}H_{20}Cl_2$						1		27.97
Phenisopham	$C_{19}H_{22}N_2O_4$	40		12					36.35
Phenkapton	$C_{11}H_{15}Cl_2O_2PS_3$		12	20	0.2		2		31.98
Phenothron I	$C_{23}H_{26}O_3$			20					32.61
Phenothrin II	$C_{23}H_{26}O_3$			12					32.91
Phenthoate	$C_{12}H_{17}O_4PS_2$		12	20	2				24.14
2-Phenylphenol	$C_{12}H_{10}O$			20					10.51
Phorate	$C_7H_{17}O_2PS_3$		2	40	0.4				13.87
Phosalone	$C_{12}H_{15}ClNO_4PS_2$	60	20	20	1		4		33.12
Phosmet	$C_{11}H_{12}NO_4PS_2$	60	12	40	1				31.57
Phosphamidon I	$C_{10}H_{19}ClNO_5P$	60	40	40			12		16.51
Phosphamidon II	$C_{10}H_{19}ClNO_5P$	40	12	12			4		18.43
Phoxim	$C_{12}H_{15}N_2O_3PS$	60	40	60	20				42.35
Pindone	$C_{14}H_{14}O_3$			12					16.40
Piperonyl butoxid	$C_{19}H_{30}O_5$			4					30.91
Pirimicarb	$C_{11}H_{18}N_4O_2$	12		20					17.85
Pirimiphos et	$C_{13}H_{24}N_3O_3PS$	20	2	20	0.4				23.04
Pirimiphos ml	$C_{11}H_{20}N_3O_3PS$	20	2	20	0.4				20.59
Prochloraz	$C_{15}H_{16}Cl_3N_3O_2$	20		40			4		36.88
Procymidone	$C_{13}H_{11}Cl_2NO_2$	12		12			1		24.44
Profenofos	$C_{11}H_{15}BrClO_3PS$		12	20	1		4	2	26.62
Profluralin	$C_{14}H_{16}F_3N_3O_4$	12		4		4			16.11
Promecarb	$C_{12}H_{17}NO_2$	12		12					13.88
Prometon	$C_{10}H_{19}N_5O$	12		40					15.10
Prometryn	$C_{10}H_{19}N_5S$	20			1				19.72
Propachlor	$C_{11}H_{14}ClNO$	20		12					12.15
Propamocarb	$C_9H_{20}N_2O_2$	12		12					8.69
Propanil	$C_9H_9Cl_2NO$	40		40			12		18.39
Propargite	$C_{19}H_{26}O_4S$			12	1				30.62
Propazin	$C_9H_{16}ClN_5$	12					2		15.50
Propetamphos	$C_{10}H_{20}NO_4PS$	20	12	12	1				16.06
Propham	$C_{10}H_{13}NO_2$	12		20					10.85
Propiconazole I	$C_{15}H_{17}Cl_2N_3O_2$	40		40			4		29.85
Propiconazole II	$C_{15}H_{17}Cl_2N_3O_2$	40		40			4		30.07
Propoxur	$C_{11}H_{15}NO_3$	20		40					12.05
Propyzamide	$C_{13}H_{11}Cl_2NO$	20		40			2		22.05
Prothiophos	$C_{11}H_{15}Cl_2O_2PS_2$		4	40	0.4		1		26.43
Prothoate	$C_9H_{20}NO_3PS_2$	20	12	12	0.4				18.66
Pyrazophos	$C_{14}H_{20}N_3O_5PS$	20	4	12	2				34.72
Pyridaben	$C_{19}H_{25}ClN_2OS$	12		40	1		2		36.34
Pyridate	$C_{19}H_{23}ClN_2O_2S$	12		20	1		2		42.46
Pyridinitril	$C_{13}H_5Cl_2N_3$	12					1		24.09

(*Continued on p. 382*)

Table 2 (*continued*)

Pesticide	Formula	Limit (ppb)							t_R (min)[a]
		N	P	O	S	F	Cl	Br	
Pyroquilon	$C_{11}H_{11}NO$	60		40					15.97
Quinalphos	$C_{12}H_{15}N_2O_3PS$	20	2	12	4				24.13
Quintozene	$C_6Cl_5NO_2$	12		12			0.4		15.74
Quizalofop ethyl	$C_{19}H_{17}ClN_2O_4$	20		20			1		39.77
Sebuthylazine	$C_9H_{16}ClN_5$	12					1		17.53
Secbumeton	$C_{10}H_{19}N_5O$	20		40					17.08
Simazine	$C_7H_{12}ClN_5$	12					2		15.04
Simetryn	$C_8H_{15}N_5S$	20			2				19.22
Sulfotep	$C_8H_{20}O_5P_2S_2$		0.4	12	0.4				13.61
Sulprofos	$C_{12}H_{19}O_2PS_3$		4	40	0.4				29.24
SWEP	$C_8H_7Cl_2NO_2$	20		12			1		15.21
Tebuconazole	$C_{16}H_{22}ClN_3O$	12		20			2		30.38
Tebutam	$C_{15}H_{23}NO$	12		12					13.75
Tecnazene	$C_6HCl_4NO_2$	12		12			1		12.05
TEPP	$C_8H_{20}O_7P_2$		2	20					11.36
Terbacil	$C_9H_{13}ClN_2O_2$	12		20			4		16.88
Terbufos	$C_9H_{21}O_2PS_3$		4	40	0.4				15.84
Terbumeton	$C_{10}H_{19}N_5O$	4		20					15.66
Terbuthylazine	$C_9H_{16}ClN_5$	12					2		15.95
Terbutryn	$C_{10}H_{19}N_5S$	12			1				20.36
Tetrachlorvinphos	$C_{10}H_9Cl_4O_4P$		12	20			1		25.53
Tetradifon	$C_{12}H_6Cl_4O_2S$			40	1		1		32.68
Tetramethrin I	$C_{19}H_{25}NO_4$	60		40					31.74
Tetramethrin II	$C_{19}H_{25}NO_4$	40		12					32.03
Tetrasul	$C_{12}H_6Cl_4S$				0.4		1		28.98
Thiobencarb	$C_{12}H_{16}ClNOS$	20		20	2		4		20.90
Thiocyclam	$C_5H_{11}NS_3$	20			0.4				10.13
Thiofanox	$C_9H_{18}N_2O_2S$	60		20	12				13.38
Thiometon	$C_6H_{15}O_2PS_3$		4	20	0.4				14.22
Thionazin	$C_8H_{13}N_2O_3PS$	12	2	20	0.4				12.06
Thiophanat ethyl	$C_{14}H_{18}N_4O_4S_2$	40		60	4				23.51
Thiophanat methyl	$C_{12}H_{14}N_4O_4S_2$	40		60	4				23.44
Tiocarbazil	$C_{16}H_{25}NOS$	12		20	1				22.00
Tolclofos methyl	$C_9H_{11}Cl_2O_3PS$		4	20	0.4		1		19.07
Tolylfluanid	$C_{10}H_{13}C_{12}FN_2O_2S_2$	12		12	0.4	12	1		23.63
Triadimefon	$C_{14}H_{16}ClN_3O_2$	12		12			2		21.77
Triadimenol	$C_{14}H_{18}ClN_3O_2$	40		20			12		24.22
Triallate	$C_{10}H_{16}Cl_3NOS$	20		20	0.4		0.4		17.00
Triamiphos	$C_{12}H_{19}N_6OP$	4	12	20					28.96
Triasulfuron	$C_{14}H_{16}ClN_5O_8S$	40		12	2		4		23.20
Triazophos	$C_{12}H_{16}N_3O_3PS$	12	12	20	1				29.39
Trichlorfon	$C_4H_8Cl_3O_4P$		12	20			1		6.86
Trichloronate	$C_{10}H_{12}Cl_3O_2PS$		4	40	0.4		0.4		22.19
Tridiphane	$C_{10}H_7Cl_5O$			20			0.4		19.50
Trietazine	$C_9H_{16}ClN_5$	12					2		16.00
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	12		12		12			13.44
Vamidothion	$C_8H_{18}NO_4PS_2$	40	20	40	4				25.40
Vernolate	$C_{10}H_{21}NOS$	20		20	0.4				9.24
Vinclozolin	$C_{12}H_9Cl_2NO_3$	20		12			1		18.88

[a]In the phosphorous trace with the higher reactant gas flow, the retention times are retarded due to lower pressure drop over the column.

GC detectors by Dressler with ±5% [29] and by Sullivan ±20% [30]. Sullivan gave a definition of practical use by combining analyte concentration with relative response. The LDR was limited to the concentration range where the response factor varies less than 20%. In our investigation the variation interval was set to ±15% in the individual element traces.

Test mixtures containing 5 to 15 pesticides were prepared in order to estimate the LDR in the individual element traces, in total 60 pesticides were carefully selected to cover all types of chemical structures. The data from these experiments were further processed with the mathematical methods for the determination of the LODs with the test pesticides [27].

The test mixtures were first prepared as stock solutions of about 100 ng of analyte in an injection volume of 2 μl which was the highest amount injected, lower concentrations down to the LOD were obtained by dilution. Calibration curves were measured with 5 to 8 concentrations depending on the detection sensitivity in the individual element trace. All values were measured as five replicates.

The evaluation of the many experimental results demonstrates that the correlation coefficient can not be used as a measure of the LDR, in particular when a large concentration range is covered.

Useful information, however, is obtained from a plot of relative response (response factor) against amount of analyte as is demonstrated with two examples in Fig. 5. The two pesticides chosen are sulfotep and ethion exhibiting both calibration functions with the lower end being linear.

The two examples sulfotep and ethion were chosen in order to show the differences in LDR which are not reflected by the correlation coefficients which were calculated with both calibration lines with a very good value of 0.9999. The advantage of demonstrating the values in the graphical plot needs no further comment. For an overview of the results in this estimation of the LDRs, the response factors were averaged and the relative standard deviation from this mean response factor was calculated for each pesticide in order to have a numerical value. With sulfotep, a relative standard deviation of 8% was obtained while for ethion it was 25%. In general, the sulfur trace was found to be the element trace

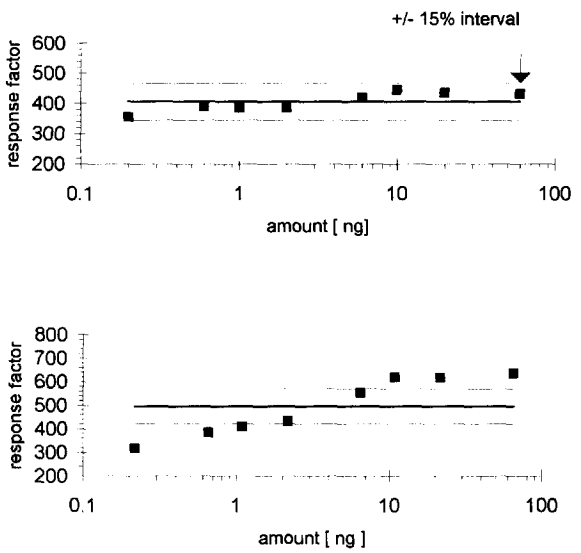

Fig. 5. LDR of sulfotep (top) and ethion (bottom) in the sulfur trace.

that showed the best detection sensitivity but also the highest variation in the LDR. On the other hand the nitrogen trace, one of the less sensitive element traces, showed lower variation in the LDR with relative standard deviations between 8 and 15%. The other individual element traces of phosphorus, fluorine, chlorine, bromine and oxygen were found at a medium position with respect to relative standard deviation of their response factors and their detection sensitivities. The detection sensitivity of an individual element trace can best be evaluated with the values compiled for all individual pesticides in Table 2. Summarizing our experience with GC–AED it can be stated that, in all individual element traces, quantification is easily possible due to the wide LDR. Reliable quantification in different concentration ranges requires the determination of a calibration curve/line with a concentration range of a factor of 50 between the lower and the upper value [27].

3.4. Determination of the LODs of 385 pesticides in residue analysis of food samples

As demonstrated, was it not feasible to determine or calculate the LODs for a great number of pesticides in all food commodities. In particular, the

theoretical approaches resulted in LODs which were not found to reflect the real situation. Therefore a straightforward practical approach was applied. Due to the high selectivity observed in all our measurements of food and also water samples, it became evident that the LOD of a pesticide in one individual element trace is almost independent of the matrix so long as the chromatographic performance is not impaired.

Applying a clean-up procedure that has been proven with many collaborative studies over the years, the recovery values of most of the pesticides have been established. Up to now, more than 400 pesticides of all pesticide classes have been investigated with the DFG multimethod S19, about 300 pesticides and metabolites have been analyzed under routine conditions with recoveries of more than 70%. The clean-up procedure has also been well established in our laboratory for many years and needs no further testing [10].

Therefore, mixtures of pesticides were prepared in concentrations of 10 μg/ml and stepwise diluted down to a concentration level of 0.1 μg/ml. The concentration levels used in the experiments are given in Table 3 together with residue concentrations in food samples processed with the multimethod S19 in the modification given in Section 2.5, the instrumental conditions are also reported in Section 2.1 Section 2.2 Section 2.3.

All the pesticides and metabolites listed in Table 2 and the six relevant PCB congeners were analyzed in all individual element traces with hot splitless injection of 2 μl.

The LOD that can be reliably achieved in routine pesticide residue analysis under the optimized parameter settings described was defined as the concentration where the analyte signal was at least three times the noise. *S/N* was not calculated by extrapolation but the lowest concentration of a pesticide that gave a peak higher than $S/N=3$ was taken as the LOD. For instance, if a pesticide produced a peak at 0.1 ng with $S/N=2$ and a peak at 0.3 ng with $S/N=5$, this higher concentration was considered as the LOD in this individual element trace. All our many analyses carried out with this method showed that a peak with a $S/N=3$ was already in the LDR and therefore suitable for quantification. The LODs of the pesticides are compiled in Table 2, the LODs of the six relevant PCB congeners were determined with 0.3 ppb for PCBs 52, 101, 153 and 1 ppb for PCBs 28, 138 and 180, respectively.

In a usual screening analysis two GC analyses per sample fraction are necessary. They cover the individual element traces of nitrogen, sulfur, phosphorus and carbon in the first run and those of chlorine, bromine and carbon in the second run. The detection in the element traces of fluorine or oxygen is normally only applied for special reasons, such as search for selected target pesticides or confirmation of suspected pesticides. The phosphorus trace must be separately applied only for quantification at lower concentration levels because the element peak can easily be detected simultaneously with sulfur and nitrogen although the conditions are not optimum with respect to the reactant gas. The LODs given in Table 2 however were measured under optimum conditions in separate runs.

3.5. Application of large-volume injection

Although the LODs compiled in Table 2 were measured with test mixtures, the values have been confirmed in many pesticide residue analyses of food samples. The confirmatory analysis of positive results from the screening was always carried out with GC–MS in the selected ion monitoring (SIM) mode applying freshly prepared calibration standards. Having completed the determination of the LODs applying hot splitless injection of 2 μl, the large volume-injection (LVI) method was developed and introduced in our laboratory [10,31]. The gain in detection sensitivity was confirmed with about 200 of the most relevant pesticides. The LODs of all pesticides were found to be improved exactly in

Table 3
Concentration levels used in experiments

Concentration in the test mixture (μg/ml)	10	5	3	1	0.5	0.3	0.1
Hot-splitless injection: 2 μl—amount injected in ng	20	10	6	2	1	0.6	0.2
Residue level in the food sample in ppb (ng/g)	200	100	60	20	10	6	2

proportion to the increased pesticide amount injected. This means that, by increasing the injection volume by a factor of 6.25, the gain in detection sensitivity was roughly six-fold. This observation was proven to be generally valid with the analysis of 412 food samples from the market during one year, namely 184 samples from vegetables and 224 samples from fruit. The monitoring resulted in 102 samples testing positive for pesticide residues, many of them containing more than one pesticide, of which many were present only at low residue concentrations. These investigations were all carried out with a modified multimethod S19 including GPC and the separation on a silica minicolumn into three fractions according to polarity as described.

The modified method with LVI results in a calculated overall increase in detection sensitivity in all individual element traces by a factor of six compared to the original method which used hot splitless injection of 2 μl. This was confirmed in many analyses of food samples and corresponding calibration mixtures and is presented with a few examples. Therefore, the LODs compiled in Table 2 were recalculated from the original values with all pesticides that have not been determined with LVI. The LODs presented reflect the detection sensitivity that can be achieved with GC–AED when using LVI with equipment that is readily available commercially.

3.6. *Influence of the gas chromatographic system on individual pesticides*

The LODs presented in Table 2 are representative for the application of the multimethod S19 with GC–AED in a general pesticide residue screening analysis of foodstuffs. They reflect the behaviour of the individual pesticides in the GC system. This is of utmost importance with many pesticides and can affect the response dramatically. There are well-known examples of pesticides that are partially or completely lost with adsorptive spots in the system or by thermal burden which can increased with deposits of matrix in the injector. Examples for such pesticides are endrin, naled, folpet and captan which, on the other hand, are well suited to check the performance of the system.

Other polar pesticides such as acephate and dimethoate show tailing on the capillary column used, with reduced peak height at low concentration levels and consequently worse detection sensitivity which would certainly be improved on an optimum separation phase. The same holds true with some late-eluting pesticides such as the labile azinphos-methyl and also mirex. These compounds can also be detected with better sensitivity when using an optimized temperature program and a shorter column.

3.7. *Detection sensitivity in the individual element traces*

Evaluating our ample stock of data, a ranking of the individual element traces according to their detection sensitivity can be given as follows: N<F<P<Br<Cl<S with nitrogen as the least and sulfur as the most sensitively detectable element. There is additionally an obvious dependence of the detection sensitivity on the structure of the molecule. In general, sulfur-containing compounds can be detected at less than 1 ng of pesticide injected. Chlorine- or bromine-containing compounds show a detection sensitivity around 1 ng. Phosphorus shows a little bit less detection sensitivity which is not in accord with the specification but was also observed by others [32]. With the element trace of nitrogen, 1 ng of triazines are easily detectable whereas with pesticides containing only one nitrogen, amounts of up to 10 ng may be necessary to obtain a suitable peak. In Table 2 the LODs for 329 pesticides are also presented in the oxygen trace, eight of those contain oxygen as the only heteroelement. The detection sensitivity of oxygen was found to be similar to that of nitrogen but its relevance in pesticide residue analysis is not yet sufficiently investigated. In a study of nitro musk residues in human fat, however, the target compounds could be detected at trace level concentrations of 20 ppb in a 1-g fat sample. The nitro musks were spotted by their nitro groups exhibiting parallel peaks in the nitrogen and the oxygen traces [33].

3.8. *Reduction of clean-up by applying multimethod S19 without silica minicolumn fractionation*

After a period with pesticide residue analysis applying GC–AED to "problem foodstuffs" that can not be analyzed with GC–ECD/NPD as described elsewhere [10], the feasibility of the elimination of

the separation step at the silica minicolumn from the clean-up procedure was investigated by analyzing spiked samples of broccoli in parallel, with and without silica minicolumn fractionation after GPC. A series of samples of 20 g of broccoli homogenate was spiked with 25 pesticides at eight concentration levels between 0.01 ppm and 0.36 ppm together with the internal standard 1,7-dibromoheptane at 0.25 ppm at all pesticide concentration levels. All samples were analyzed without silica minicolumn fractionation as triplicates. The parallel analyses using the silica minicolumn fractionation were carried out with the addition of the same pesticide mixture at 0.2 ppm also in triplicate. In this series of experiments the final extract was concentrated by rotary evaporation to 1 ml and 12.5 μl were applied with LVI. In Fig. 6, the results of the comparative experiments are presented as chromatograms with the individual element traces of carbon for the inspection of the distribution of the matrix burden and of chlorine to see the selectivity and the gas-chromatographic performance. It can be easily recognized from the chromatograms of the carbon trace that the matrix compounds are mainly present in fractions 1 and 2 and that the matrix is nearly additive, as expected. The same holds true for the chlorine trace chromatograms. The addition of the chromatograms of fractions 1 and 2 would result in the chromatogram of the non-treated sample shown at the top.

The pesticides selected for spiking include active ingredients applied to growing broccoli and pesticides that are known to be prone to degradation in the GC system. Additionally, the pesticides should represent the whole GC elution profile and include two critical pairs that can be independently determined by their different individual element traces.

In general the recoveries were found to be acceptable with most of the pesticides, trifluralin and methidathion could not be detected down to the 0.01 ppm residue level with the extract diluted five-fold compared to the optimized procedure. Methamidophos, chlorpropham, chlorthalonil and dichlofluanid show mean recoveries below the generally accepted 70%. Captan and dicofol recoveries

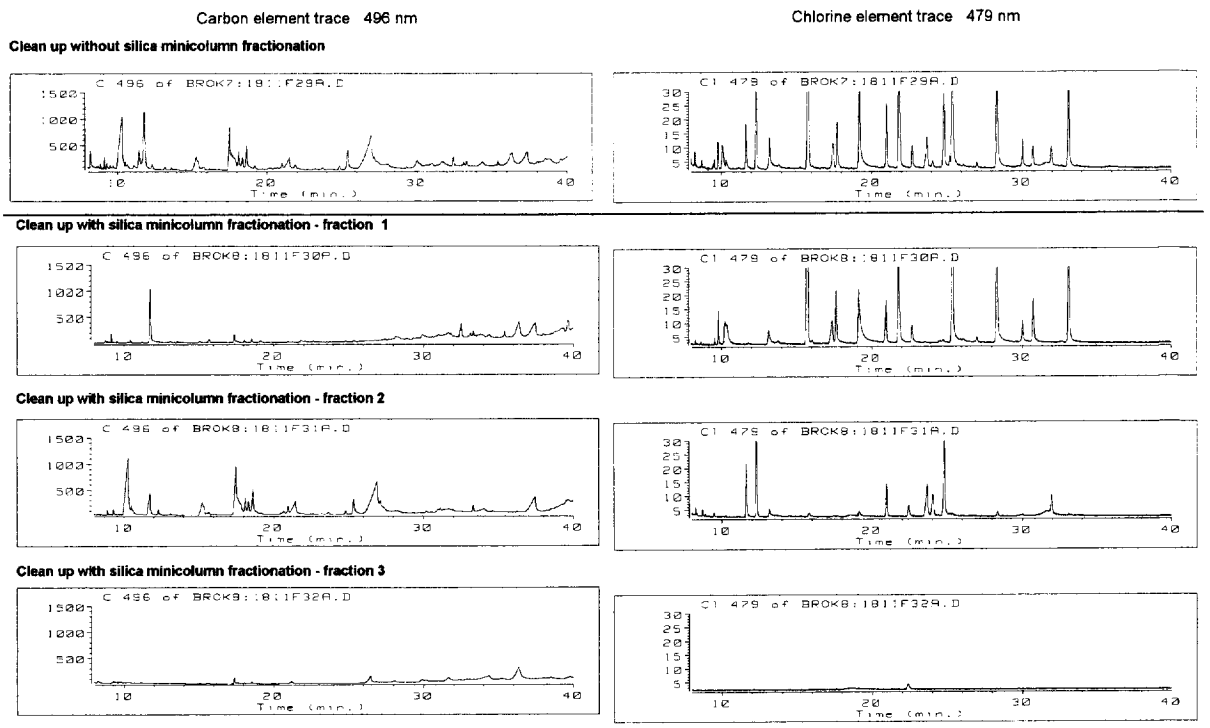

Fig. 6. Comparison of clean up with and without silica minicolumn fractionation.

were found to decrease with the progress of the series of analyses. This is certainly the result of the accumulation of matrix deposits in the injector. This observation is in full agreement with long-term experience with these vulnerable compounds. The recovery data and their evaluation are presented in detail elsewhere [27,28].

The problems with pesticide loss in the screening analysis increase when the extracts are reduced to a final volume of 200 μl as is necessary with many

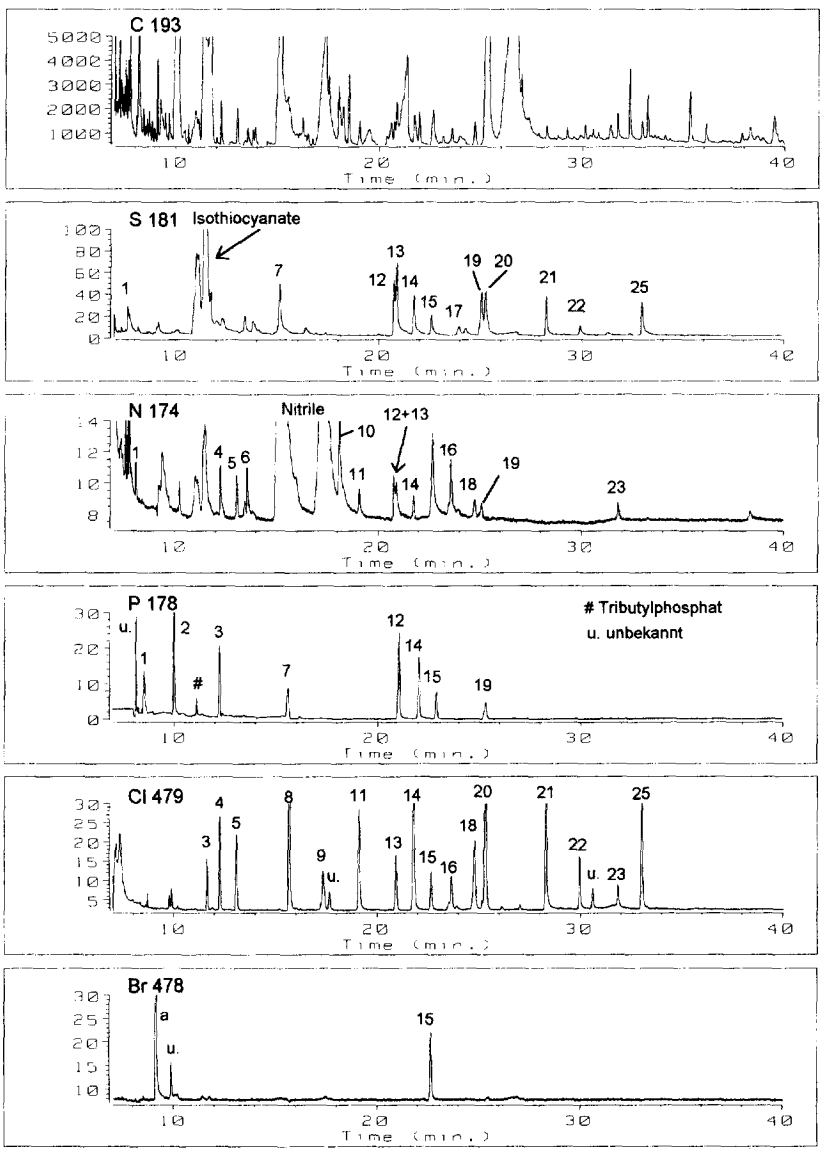

Fig. 7. GC–AED chromatograms of broccoli spiked with 25 pesticides at 0.12 ppm; individual element traces as indicated. 1=methamidophos; 2=mevinphos; 3=heptenphos; 4=propachlor; 5=chlorpropham; 6=trifluralin; 7=dimethoate; 8=lindane (γ-HCH); 9=chlorothalonil; 10=pirimicarb; 11=vinclozolin; 12=pirimiphosmethyl; 13=dichlofluanid; 14=chlorpyrifos; 15=bromophos; 16=metazachlor; 17=captan; 18=procymidone; 19=methidathion; 20=α-endosulfan; 21=β-endosulfan; 22=endosulfan sulfate; 23=iprodione; 24=dicofol; 25=tetradifon; a=1,7-dibromoheptane.

pesticides to achieve the critical 0.01 ppm residue level. The feasibility was again investigated with spiked samples of broccoli containing 0.12 ppm of the same 25 pesticides that were applied in the recovery experiments reported above.

A complete analysis is shown in Fig. 7 with the six individual element traces recorded in the routine pesticide residue analysis. The carbon trace shows the bulk of matrix in such an extract whereas the individual element traces of phosphorus, chlorine and bromine exhibit almost no peaks apart from those originating from pesticide residues. With vegetables of the brassica family, isothiocyanates and nitriles are found in the volatile fraction that can be detected by GC, therefore a few peaks are observed in the sulfur trace and the nitrogen trace as indicated in the corresponding chromatograms. Summarizing, most of the pesticides can be detected with the exception of dicofol and captan as already explained.

Finally, the obvious problems with pesticide loss in the screening analysis when running a series of samples in automated pesticide residue analyses should be addressed. In Fig. 8 two chromatograms are presented from the course of the recovery analyses. For reasons of simplicity, only the element trace of chlorine is shown. In the upper chromatogram one analysis recorded at the beginning of the series with a clean injector and new retention gap is shown while in the lower chromatogram one analysis after 15 injections in the series, that means with the matrix burden of 15 broccoli extracts is shown. As expected, the pesticides prone to degradation were found with decreasing recoveries or almost lost as observed with dicofol and captan, to name the most prominent compounds of this type. These chromatograms demonstrate clearly the reality of the daily pesticide residue screening and the necessity of permanent careful checking of the performance of the GC system by analyzing standard test mixtures between the samples. The repeat of the analysis after cleaning the system resulted in a similar chromatogram to that shown in the upper trace.

Summarizing, the modification of multimethod S19 by omitting the silica minicolumn fractionation and taking advantage of the high element selectivity of AED has been proven to work well in our laboratory over a period of time. No differences were found between the results obtained with fractionation and without fractionation on the silica minicolumn with respect to detection sensitivity and cross selectivity. The gas-chromatographic performance was not found to be impaired by the higher concentration of matrix compounds and the standing time of the instrument was not reduced with respect to the throughput of food samples. This can be understood from the fact that the overall load of the injector and retention gap with matrix compounds from one food sample by introducing the extract from GPC directly is not higher than that after the silica minicolumn fractionation. The only difference between the two methods is that the matrix burden is either introduced at once or distributed into three parts with successive injections. The most important point to stress is the gain in productivity in the laboratory that is achieved

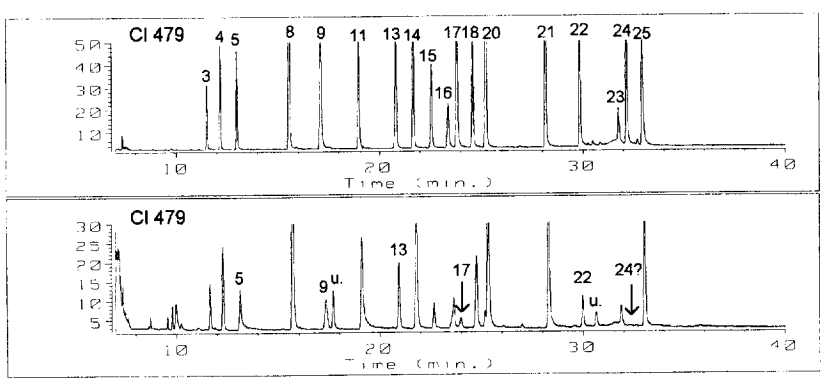

Fig. 8. GC–AED chromatograms of broccoli spiked with 25 pesticides at 0.12 ppm in the course of automated analyses—chlorine trace. Top: clean GC system, bottom: after a series of 15 injections; for pesticide numbers see Fig. 7.

by the reduction of the number of parallel runs in a usual screening analysis to two injections per food sample.

4. Conclusion

The value of a detector in pesticide residue analysis can be determined by the criteria selectivity/specificity, reliability, sensitivity, quantitative response and the information that is provided. The final proof is the productivity that can be achieved in the laboratory doing the daily pesticide screening analysis.

4.1. Selectivity/specificity

AED enables the detection of all pesticides by their heteroatoms with high selectivity. The AED chromatograms of the various heteroatomic traces from food samples show hardly any peaks resulting from coextracted matrix compounds thus allowing easy identification of pesticide residues. There are, however, exceptions with a few "problem foodstuffs" such as onion, garlic, leek and plant foodstuffs from the brassica family which contain sulfur compounds and also nitrogen compounds such as nitriles and isothiocyanates that produce peaks in the individual element traces. They may dominate the chromatograms, overlapping the pesticides such that the sulfur trace is of little use for pesticide residue analysis in onion, garlic and leek. However, the analysis in the other heteroelement traces is not impaired.

4.2. Reliability

The confirmation of elemental identity can be performed down to the lowest residue levels by inspecting the partial emission spectra recorded during the GC run (snap shot). According to our experience cross selectivity is very seldom found with pesticide residue analysis of plant foodstuffs.

4.3. Sensitivity

Detection sensitivity varies with the elements and is not as good as with other selective detectors for nitrogen. The high element specificity, however, compensates for this lack of sensitivity because it allows higher concentration of the sample extracts in the clean-up procedure.

The extract from 10 g of fruit or vegetable can be concentrated to 200 μl and applied to Large Volume Injection into a cold PTV injector with solvent venting. This was successfully carried out with an injection volume of 12.5 μl using a commercial autosampler.

LODs were determined for 385 pesticides and metabolites with each heteroatom under conditions of daily routine residue analysis in food samples. All pesticides could be detected down to 10 μg/kg (0.01 ppm) when using LVI. The great majority of the pesticides could also be detected at least in one element trace by using "hot splitless" injection of 2 μl down to the critical 0.01 ppm concentration level.

4.4. Quantitative response

Quantification with AED was found to be easy and exact, because all heteroatomic traces exhibit a wide linear dynamic range that reaches down to the minimum residue levels.

4.5. Information

AED is the only detection which provides tentative information on the elemental composition of the detected compound. Usually the type of heteroatoms and their relative proportion in a molecule is presented. This information on suspect pesticides contributes substantially to their identification in the screening analysis with GC–AED and is complementary to the final confirmatory analysis with GC–MS.

4.6. Productivity

With the reduced clean-up procedure, it is possible to screen for pesticides with two GC runs for one food sample whereas with other selective detectors with many plant foodstuffs a separation into three fractions and three corresponding runs is required.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

References

[1] A.J. McCarthy, S.J. Tong and W.D. Cook, Anal. Chem., 37 (1965) 1470.
[2] C.A. Bache and D.J. Lisk, Anal. Chem., 37 (1965) 1477.
[3] B.D. Quimby and J.J. Sullivan, Anal. Chem., 62 (1990) 1027.
[4] J.J. Sullivan and B.D. Quimby, Anal. Chem., 62 (1990) 1034.
[5] P.C. Uden, J. Chromatogr. A, 703 (1995) 393.
[6] S.M. Lee and P.L. Wylie, J. Agric. Food. Chem., 39 (1991) 2192.
[7] H.-J. Stan and M. Linkerhägner, in P. Sandra and G. Devos (Editors), Proceedings of the 15th International Symposium on Capillary Chromatography, Riv del Garda, 1993, Huethig, Heidelberg, 1993, p. 1257.
[8] H.-J. Stan and M. Linkerhägner, J. High Resolut. Chromtogr., 16 (1993) 539.
[9] M. Linkerhägner and H.-J. Stan, Dtsch. Lebensm.-Rundsch., 89 (1993) 143.
[10] M. Linkerhägner and H.-J. Stan, Z. Lebensm.-Unters.-Forsch., 198 (1994) 473.
[11] H.-J. Stan and M. Linkerhägner, Vom Wasser, 79 (1992) 75.
[12] E.C. Goosens, D. Dejong, G.J. Dejong, F.D. Rinkema and U.A.Th. Brinkman, J. High Resolut. Chromatogr., 18 (1995) 38.
[13] T. Hankemeier, A.J.H. Louter, F.D. Rinkema and U.A.Th. Brinkman, Chromatographia, 40 (1995) 119.
[14] F.D. Rinkema, A.J.H. Louter and U.A.Th. Brinkman, J. Chromatogr., A, 678 (1994) 289.
[15] R. Eisert, K. Levsen and G. Wünsch, J. Chromatogr. A, 683 (1994) 175.
[16] H.-J. Stan (Editor) Analysis of Pesticides in Ground and Surface Water I, Progress in Basic Multi-Residue Methods, Chemistry of Plant Protection, Vol. 11, Springer, Berlin, 1995.
[17] H.-J. Stan (Editor) Analysis of Pesticides in Ground and Surface Water II, Latest Developments and State-of-the-Art of Multiple Residue Methods, Chemistry of Plant Protection, Vol. 12, Springer, Berlin, 1995.
[18] B.F. Scott and P.L. Wylie, in H.-J. Stan (Editor), Analysis of Pesticides in Ground and Surface Water II, Chemistry of Plant Protection, Vol. 12, Springer, Berlin, 1995, p.33.
[19] H.-J. Stan and M. Linkerhägner, in H.-J. Stan (Editor) Analysis of Pesticides in Ground and Surface Water II, Chemistry of Plant Protection, Vol. 12, Springer, Berlin, 1995, p.59.
[20] H.-P. Thier and H. Zeumer (Editors) Manual of Pesticide Residue Analysis, Volume 1, Multimethod S19, DFG Deutsche Forschungsgemeinschaft. VCH, Weinheim, 1991.
[21] D.L. Massart in, D.L. Massart (Editor), Evaluation and Optimization of Laboratory Methods and Analytical Procedures, Elsevier, Amsterdam, 1978.
[22] H.B.S. Conacher, J. Assoc. Off. Anal. Chem., 73 (1990) 332.
[23] G.A. Parker, J. Assoc. Off. Anal. Chem., 74 (1991) 868.
[24] H. Kaiser, in H. Kaiser (Editor), The Limit of Detection of a Complete Analytical Procedure, Adam Hilger, London, 1968.
[25] J.C. Miller and J.N. Miller, in J.C. Miller and J.N. Miller (Editors), Statistics for Analytical Chemistry, Ellis Horwood Limited, Chichester, 1984.
[26] H.-P. Thier and J. Kirchhoff (Editors) Manual of Pesticide Residue Analysis, Volume 2, Multimethod S19, DFG Deutsche Forschungsgemeinschaft. VCH, Weinheim,1992, p.3.
[27] M. Linkerhägner, Thesis, Technical University Berlin, 1994.
[28] http://www.stanpc1.lb.tu-berlin.de/lc/stanpapergcaed
[29] M. Dressler, in M. Dressler (Editor), Selective Gas Chromatographic Detectors (Journal of Chromatography Library, Vol. 36), Elsevier, Amsterdam, 1986.
[30] J.J. Sullivan, in R.L. Grob (Editor), Modern Practice of Gas Chromatography, Wiley, New York, 1977, Ch. 5, p. 219.
[31] H.-J. Stan and M. Linkerhägner, J. Chromatogr. A, 727 (1996), 275.
[32] H. Köhle, F. Karrenbrock and K. Haberer, Wasser, Boden, Luft und Boden, 6 (1990) 16.
[33] M. Linkerhägner, H.-J. Stan and G. Rimkus, J. High Resolut. Chromatogr., 17 (1994) 821.