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CAPA — COMPUTER AIDED PESTICIDE ANALYSIS

COMPUTER PROGRAM FOR THE AUTOMATED EVALUATION OF CHROMATOGRAPHIC DATA FOR RESIDUE ANALYSIS OF FOODS

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SUMMARY

Pesticide residue analysis in food by means of gas chromatography with columns of different polarity and several selective detectors provides the analyst with a great number of chromatographic data. The introduction of personal computer based chromatographic data systems into research laboratories increased the efficiency of information management and organization; user designed software packages now have direct access to the stored data. The computer program CAPA (Computer Aided Pesticide Analysis) was developed for the interpretation and evaluation of chromatographic results. The program is written in TURBO PASCAL 3.0 and consists of several subprograms. In the main database all pesticides are filed in a multidimensional structure. The various subprograms have access to this catalog of retention and response data. Using the subprogram INTERPRET, which is the core of CAPA, the analyst is provided with all information necessary to interpret a gas chromatogram: identification of calibrated pesticides and estimation of their concentration. Automated screening analyses can be evaluated with the subprogram AUTOINTERPRET, an automated version of INTERPRET that uses all relevant information stored in the data base. A report is produced containing the pesticides found in the sample and proposals how to confirm them best with the equipment and methods available. Finally the analyst has to make the decision about the probable presence and quantity of the indicated pesticides and to project the next confirmatory step by using INTERPRET.

INTRODUCTION

Multi-residue pesticide analysis is performed on a whole range of foods with the use of standardized extraction and clean-up procedures, which means that the clean-up procedures must remove a multitude of matrix compounds from about 100 types of food. At the same time, the clean-up procedures must not remove any of the more than 200 pesticides that can be analysed by capillary gas chromatography. The great extent to which the clean-up procedures now in use fulfil this requirement in combination with gas chromatography using selective detection is surprising.

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The analysis of any food taken to the laboratory starts with weighing a representative sample and ends in injecting the cleaned extracts from a small vial into a gas chromatograph equipped with a suitable capillary column and selective detectors. The first visible results are gas chromatograms and lists of retention times and peak areas calculated by means of integrators. In a modern laboratory, gas chromatographs and personal computers can be found close together. Personal computers are versatile tools that may serve many jobs, one major application in a laboratory being to replace older, less flexible integrators. In recent years, various commercial chromatography software systems have proved their excellence in daily routine work. The design of earlier software packages was more hardware oriented in order to gain maximum efficiency from a limited configuration with respect to the central processing unit and the internal and external memory capacity.

The entry of the major computer companies into the market accelerated the progress of the development of both personal computer hardware and software. An industrial standard was established with the series of Intel microprocessors from 8088 to 80386 and the operating system MS-DOS. A multitude of software packages were designed or adapted for the new standard configuration, covering all kinds of applications from the office to the research laboratory. The chromatography software followed this line.

Chromatography programs acquire and process raw data from any chromatographic detector by applying flexible, sophisticated algorithms. Peak detection and peak-area calculation can be manipulated by means of parameter setting with direct control on the computer screen. By this means, optimization of chromatographic parameters is an easy task. The results are stored in standardized file formats, and they are therefore accessible by other programs implemented under the same operating system.

The commercial chromatography software is optimized for the precise calculation of retention times and the areas of specified peaks or clusters. By means of calibration mixtures the recognition of a series of compounds and their quantitative determination are possible. The common methods are external and internal standardization. These software packages do not address the problems that are typical of environmental analysis or pesticide residue analysis of foods.

Our aim was to develop a software package that supports the analyst in daily routine work in a pesticide residue laboratory. It includes the ideas from previous programs that addressed the difficulties arising from interfering matrix compounds, MATRIXCOMP[1], and a precursor of Computer Aided Pesticide Analysis (CAPA) called INTERPRET[2].

METHODS

After a standardized clean-up[3], the determination of pesticide residues in foods is performed by using various gas chromatographs with capillary columns and effluent splitting to two selective detectors. Combinations of an electron-capture detector and a flame photometric detector[4] and of an electron-capture detector with a nitrogen–phosphorus detector[5] are used. Capillary columns of various lengths between 10 and 50 m and inner diameters of 0.2 and 0.32 mm may be connected to hot splitless, on-column or cold splitless injectors. For screening analysis, long columns

coated with non-polar stationary phases such as SE-30, SE-52, SE-54 or OV-1 are used. Confirmatory analyses are performed on shorter columns coated with OV-1701, OV-17, Carbowax or OV-225.

The signals from the detectors are transferred via an analog-to-digital converter to a Trilab 2000 microcomputer system (Trivector, Niederolm, F.R.G.) or a personal computer (IBM-XT) working with a Nelson 3000 Series chromatography data system (Nelson Analytical, Cupertino, CA, U.S.A.), automatically processed by the manufacturer's software packages and stored as raw data and result files on 20-Mbyte hard disks.

The result files are transferred via RS232C interfaces to a central personal computer (IBM-AT) with a 40-Mbyte hard disk, where the interactive data evaluation and chromatogram interpretation are executed by means of our new user-designed software package CAPA.

COMPUTER CONFIGURATION AND DATA EXCHANGE

The Trilab 2000 chromatography data system incorporates a visual display unit (VDU), 288-kbyte RAM and two floppy disk drives (each with 640 kbyte). The Trilab 2000 is linked to a Sichromat 2 gas chromatograph (Siemens, Karlsruhe, F.R.G.) for two-dimensional analysis[6] by means of a special interface board. This permits parallel transfer of digital data from two detector channels to the computer and the control of all instrument parameters by computer programs. The system also includes a software package for evaluating all kinds of chromatographic data files and a BASIC interpreter.

The Nelson chromatography data system consists of an IBM-XT with 512-kbyte RAM, 20-Mbyte hard disk and a single floppy disk drive (360 kbyte). The IBM-XT communicates via an IEEE-488 board and three Nelson Interface boxes with three HP5890 gas chromatographs (Hewlett-Packard, Palo Alto, CA, U.S.A.), each containing two selective detectors.

These two computers serve mainly for data acquisition and chromatogram processing. The result files are transferred automatically to the IBM-AT by means of small programs written in BASIC and ASSEMBLER, respectively.

The IBM-AT is configured with 640-kbyte RAM, 40-Mbyte hard disk, a single floppy disk drive (1.2 Mbyte) and two monitors. One is a high-resolution screen for alphanumeric data and the other a low-resolution screen for graphical display.

PROGRAM

The program CAPA is written in TURBO-PASCAL 3.0 and works under MS-DOS; it requires 640 kbyte of RAM and a hard disk. The program is of modular structure, several modules being written in ASSEMBLER in order to accelerate time-consuming procedures. Communication and data exchange with the chromatography systems are performed by means of a memory resistant ASSEMBLER program, which executes data exchange in the background.

CAPA consists of three major programs: EDITOR, INTERPRET and AUTOINTERPRET.

EDITOR is used for creating a relational database that contains all chro-

matographic data about the calibrated pesticides and documented matrix compounds from food samples. This database forms the foundation for the use of the other two programs.

INTERPRET is designed for interactive evaluation of gas chromatograms obtained by standardized analytical procedures. Its special feature is the close link to the problems evolving from the multitude of pesticides and environmental contaminants that might be found in small amounts in the analysed food. The program is useful for both screening and confirmatory analysis.

AUTOINTERPRET is the automated version of INTERPRET. After evaluating the screening analysis, it produces a report about the possible contaminants in the food sample. This report includes advice about how best to achieve confirmation by means of the available analytical instruments.

The three major programs are composed of subprograms that can be addressed from the displayed menu by pressing function keys.

Starting with the EDITOR menu (Fig. 1), twelve subprograms are presented on the screen. This list gives an impression of the volume and the structure of the data base. The entries are compiled in various catalogs, which will be explained briefly. As is usual in recent program design, all the subprograms are selected by means of cursor marking. The subprograms present tables on the screen similar to the popular spreadsheets, with a list of the actual function key set.

The CATALOG OF CALIBRATED PESTICIDE DATA is the main database. All pesticides with all their calibrated data sets are filed in a multi-dimensional structure. This means that all retention times measured on various columns under standard conditions and response values calculated for individual selective detectors are retained under the particular pesticide name. A schematic plot of the structure is given in Fig. 2.

The CATALOG OF MATRIX SAMPLES contains all data about interfering substances from background chromatograms. These substances passing through the

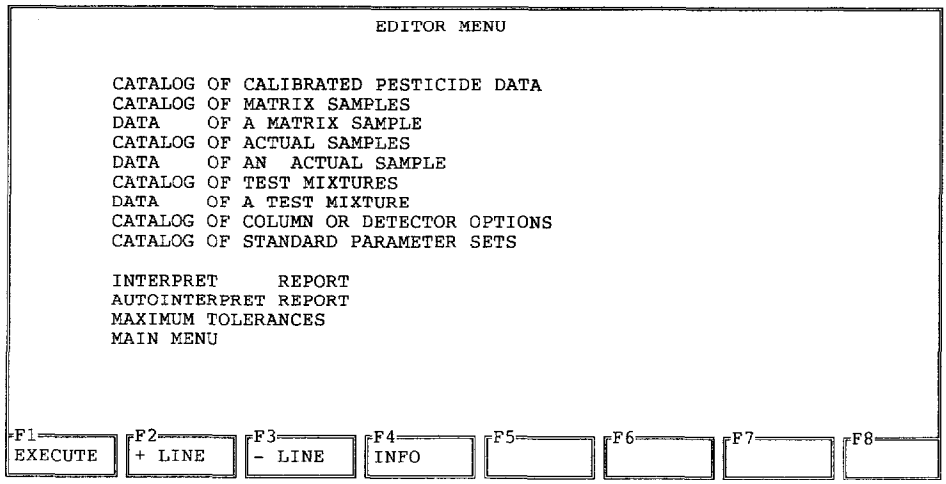

Fig. 1. Editor menu.

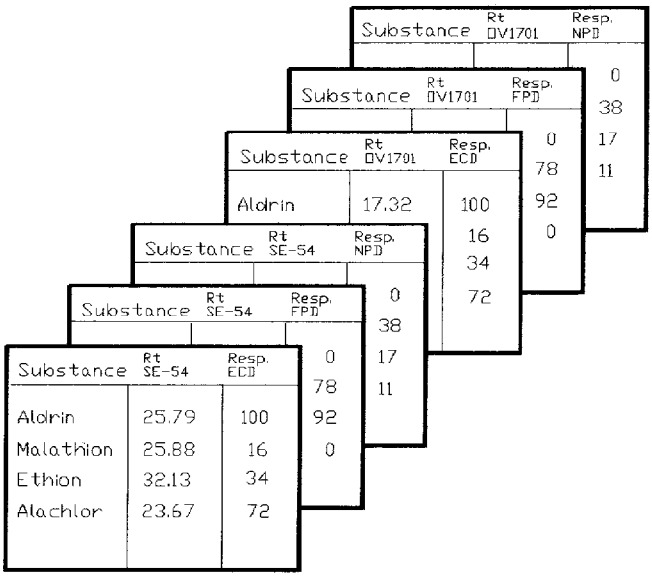

Fig. 2. Multi-dimensional structure of the database.

clean-up procedure together with pesticides vary considerably with the type of food being analysed. Although the provenance might be different, background peaks produced by the same type of food show sufficient resemblance. All peaks that cannot be identified as a pesticide residue in an extract with our gas chromatographic methods are cataloged as matrix compounds. The list of matrix compounds includes many plasticizers and other environmental contaminants. The catalog is constructed in the same way as the catalog of pesticides.

The CATALOG OF ACTUAL SAMPLES must be created to describe the food samples that are actually analysed in the laboratory. Each sample is described as a set of individual entries using a special template in which all retention times and areas of all peaks recorded by selective detectors are entered. This may be executed off-line via the keyboard or by on-line data transfer from the corresponding detector channels. The set of entries consists of several parts if the clean-up procedure produces more than one fraction from the same food sample. Each fraction is individually analysed with the gas chromatographic system and compared with a pesticide subcatalog corresponding to the individual fractions. The templates for the entries of actual samples and matrix samples are identical, which permits the transfer of actual sample entries into the catalog of matrix samples after having been confirmed as uncontaminated with any of the calibrated pesticides. In this way the catalog of matrix samples is easily upgraded to the actual situation by overwriting older references from the same type of food.

The CATALOG OF TEST MIXTURES was established to control the actual gas chromatographic conditions. These test mixtures vary with the type of food and must fit the selected gas chromatographic system. It is essential to analyse at least one test mixture together with each series of samples. INTERPRET cannot be started

to evaluate the analysis of food samples without having performed a recalibration of the data in the pesticide catalog by means of the data from an actual test mixture chromatogram.

The subprograms SETS and OPTIONS are designed for describing the various gas chromatographic systems in use. Standardized methods are named with an alphanumeric code, so it is necessary that the user tells the system under which conditions the samples have been analysed by entering the correct code. An erroneous input at this stage would cause considerable trouble but is immediately indicated when the test mixture is used for recalibration. The program responds with an error message.

The subprogram MAXIMUM TOLERANCES contains a compilation of maximum tolerances established in Germany. It can be activated directly from INTERPRET and entries can be transferred to the report. As an extra, the structural formulae of the pesticides are provided on a second screen page.

The INTERPRET REPORT subprogram is designed to record the decisions made by the analyst during the session with INTERPRET. The AUTOINTERPRET REPORT subprogram is the corresponding part of AUTOINTERPRET.

Fig. 3 shows part of the main catalog of pesticides. Pesticides are described by their common name, retention times, response factors, information from the clean-up procedures and the concentrations used for calibration. Scrolling through the catalog is possible in various directions by means of the command keys shown in the bottom line. Moving the cursor up and down is executed by pressing F3 and F4. Scrolling can be speeded up with paging by means of F5 and F6.

When marking the column or the detector row with the cursor, the command keys F8 and F9 call up retention times calibrated with another column or the response factors of another detector.

The structure of the database is shown in Fig. 1.

RETENTION TIMES AND RESPONSE FACTORS

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NR	SUBSTANCE	Rt (min) COLUMN A-SE54	RESPONSE DETECTOR A-ECD	%/FRACT 1	ug/ul
97	DISULFOTON	20.180	-1	0.0	0.010
98	DELTA-HCH	20.323	4999	100.0	0.010
99	DICHLONE	20.570	570	0.0	0.010
100	ETRIMFOS	20.620	109	0.0	0.010
101	TRIALLAT	20.670	350	0.0	0.010
102	CHLOROTHALONIL	21.120	1000	0.0	0.010
103	FORMOTHION	21.830	2035	0.0	0.010
104	DESMETRYN	22.120	-1	0.0	0.010

F1 HOME | F2 HELP | F3 - LINE | F4 + LINE | F5 - PAGE | F6 + PAGE | F8 OPT <-- | F9 OPT -->

Fig. 3. Catalog of calibrated pesticide data. Left column: pesticide number. Second column: pesticide name. Third column: retention time (min) measured on an SE-54 capillary column. Fourth column: ECD response value. The value −1 is given to all pesticides that are not yet calibrated. Fifth column: retrieval in the clean-up fraction. Last column: amount of substance which yields the displayed response.

APPLICATION

The core program is INTERPRET, and how this program is used can be best demonstrated by applying it to an analysis of a real food sample.

First we have to enter the sample name, the number of the fraction, the final concentration in the cleaned extract and the injection volume into the catalog of actual samples. All gas chromatographic data from this sample are filed closely related to this table. The data set is activated by marking the sample line with the cursor and pressing the TAB key. This activates the work sheet of INTERPRET containing the data for the actual sample. We have now reached the stage of interactive chromatogram interpretation (Fig. 4).

The work sheet consists of three windows and two headlines. The first headline indicates the actual sample and the second the corresponding matrix sample. The catalog of sample data is presented in the first window and in the second window the corresponding part of the main catalog of calibrated pesticides is provided. The program automatically extracts the background chromatogram produced by the same type of food with identical origin and clean-up fraction from the catalog of matrix samples and lists the matrix peaks in the bottom window. The important feature of INTERPRET is the link between the three catalogs presented in the three windows.

Evaluation of chromatograms is performed by parallel scrolling through the three catalogs with the sample catalog being the leader. This happens in the following way: the cursor is set to any peak in the sample window and immediately the middle window presents the corresponding part of the main catalog which contains four pesticides with similar retention times to that of the marked peak. The pesticide which fits best is highlighted. In our example we moved the cursor to peak 9 in the sample window and, consequently, DDT was indicated in the pesticide window. At the same time peak 8 was marked in the matrix window. Comparing the retention times in all three catalogs we came to the conclusion that peak 9 in the sample resembles more the matrix peak than the pesticide DDT.

If we now move the cursor to peak 5, for instance, the contents of windows 2 and 3 change automatically (Fig. 5). They now present peak data corresponding to the retention time of peak 5. In the pesticide catalog endosulfan-I is indicated, which exhibits a very similar retention time. None of the matrix compounds resemble peak 5. Looking at the second detector, the NPD, shows that there is no response. This agrees also with endosulfan. Here we can make use of the simultaneous display on the graphical monitor (Fig. 4b).

The graphical screen is divided horizontally into three parts, each designed to display a signal trace from a detector. There are several options in using the graphical monitor, one being demonstrated in Fig. 4b, the parallel display of two selected detector recordings from the same chromatogram in the two upper sections plus one trace from a corresponding matrix chromatogram. Other options include the simultaneous display of three chromatograms from the same detector with one trace from the actual sample, the second from the corresponding matrix and the third from the calibrated pesticide catalog. The signal traces may be displayed from raw data or condensed data, depending on the mode of acquisition. When no such chromatographic data are stored, the displayed chromatograms are reconstructed from the cataloged retention times and response factors. This applies to all graphical displays of calibrated pesticides, which generally are not stored as original raw data.

(a)

Nr	actual sample		fr	country	date	mg	samp/ul	i. vol. ul
1		RADISH	1	NETHERLANDS	1.9.87		5.00	1.0
lNr	matrix sample		fr	country	date	mg	samp/ul	i. vol. ul
2		RADISH	1	NETHERLANDS	25.5.87		5.00	1.0

Nr	compound	Rt	A-SE54 resp	A-ECD	%Fr1	
9	PEAK 9	32.941	98.0039	-1		
10	PEAK 10	36.803	37	-1		ACTUAL
9	PEAK 9	32.941	98	-1		SAMPLE
0		0.000	0	-1		DATA

Nr	pesticide	Rt	A-SE54 r/ng	A-ECD	%Fr1	conc. ppm
205	DDT	32.951	206	100		0.095
206	CYANOFENPHOS	33.000	77.0000	0		0.255
207	ENDOSULFANSULFAT	33.120	0	0		0.000
208	DICOFOL	33.754	19.5713	30		1.002

Nr	compound	Rt	A-SE54 resp	A-ECD	%Fr1	
9	PEAK 8	32.938	84.4861	80		
10	PEAK 9	34.109	21	50		MATRIX
0		0.000	0	-1		SAMPLE
0		0.000	0	-1		DATA

F1 HOME | F2 CHROM. | F3 - LINE | F4 + LINE | F5 - WINDOW | F6 + WINDOW | F7 LIMITS | F8 OPTIONS

(b)

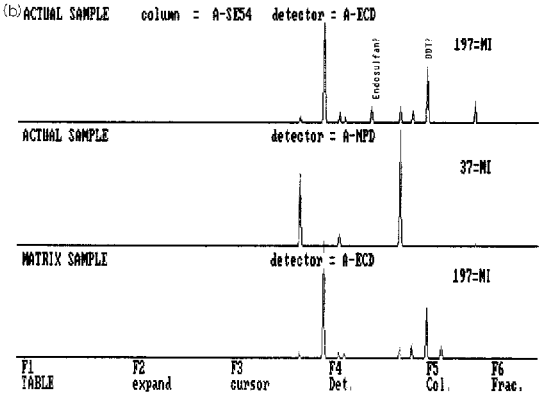

Fig. 4. Central work sheets of INTERPRET. (a) INTERPRET work sheet on the alphanumeric screen. Header: general information about the actual and the corresponding matrix sample, including sample number, sample name, clean-up fraction, origin, date of analysis, sample concentration of the injected extract and injection volume. Top window: chromatographic data for the actual sample, including peak number, peak name, retention time on an SE-54 capillary column, ECD response value, recovery of a sample compound in the first clean-up fraction (−1 means that the value is unknown); peak 9 is in progress. Middle window: chromatographic data for calibrated pesticides, including number and name of the substance, retention time on an SE-54 capillary column, ECD response, recovery in the first clean-up fraction, estimated residue concentration for the case when the indicated peak proved to be the calibrated pesticide. Bottom window: chromatographic data for the corresponding matrix sample, including peak number, peak name, retention time on an SE-54 capillary column, ECD response value, recovery of a sample compound in the first clean-up fraction (−1 means that the value is unknown). (b) Chromatograms from radishes. Top: ECD chromatogram from the actual sample. Middle: NPD chromatogram from the actual sample. Bottom: ECD chromatogram from a corresponding matrix sample. Scrolling through the peak table of the actual sample or moving a thin vertical line over the chromatograms on the graphical screen causes the computer to search for and highlight those pesticides and matrix peaks which fit best with the indicated sample peak.

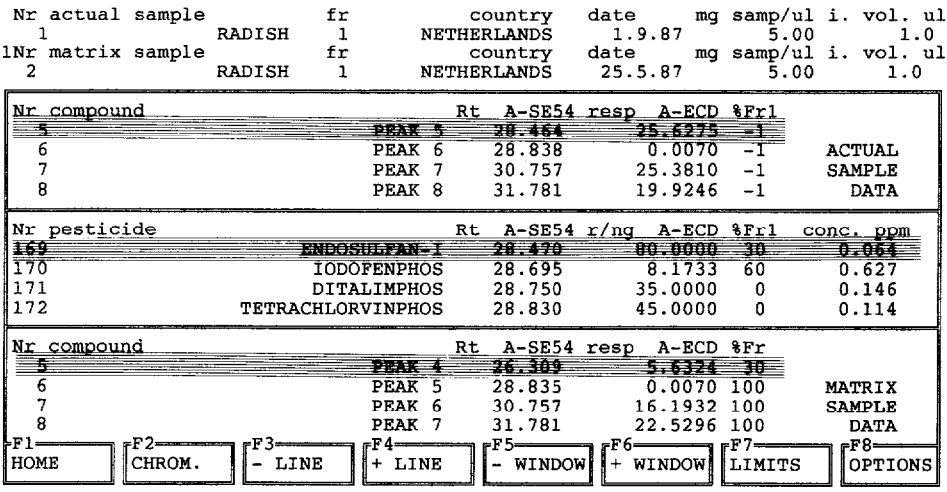

Fig. 5. Central work sheet of INTERPRET. The figure reflects the situation when sample peak 5 is being processed.

The graphical display offers chromatogram spreading with automatic normalization to the largest peak. When moving the cursor (a thin vertical line) through the chromatograms, the extracts in the three windows of the alphanumeric screen scroll simultaneously. In this way the retention time of an indicated peak can be seen in the sample window as a highlighted line. At the same time, the best fitting peaks in the other window are also highlighted as described.

Inspecting the actual chromatograms on the graphical screen we see no peak on the NPD trace at the retention time of peak 5 and no peak on the ECD trace of the matrix that may be mistaken for endosulfan-I. This result was confirmed by the presence of the isomer endosulfan-II, which always appears together with endosulfan-I. Additionally these two peaks were identified using a capillary column of different polarity.

The next question that arises is how the concentration of this pesticide residue is related to the maximum tolerance limit. The last row of the pesticide catalog provides the concentration calculated for the corresponding peak. In our example we see 0.064 ppm. This means that if peak 5 in the sample is really endosulfan-I then its concentration is calculated from the stored response values as 0.064 ppm (Fig. 5).

Pressing the command key F7 (LIMITS) takes us directly to the appropriate reference in the list of maximum tolerances. A listing of the maximum tolerances established for the different kinds of food appears on the screen. The analyst now selects the right type of food and indicates it with the cursor. The final step of working with INTERPRET is making the decision about the investigated analytical response in the chromatogram of the food sample by means of a command key. There are three options explained in a window opened by the report key:

F4 = IDENTIFIED means the pesticide residue is considered to be identified with sufficient reliability. No further confirmation is required.

F5 = CONFIRMATION FOR IDENTIFICATION REQUIRED means the

presence of the pesticide residue cannot be excluded but its identity is uncertain and must be elucidated by means of data from gas chromatography or mass spectrometry.

F6 = CONFIRMATION FOR QUANTIFICATION REQUIRED means the identity of the pesticide residue is considered to be sufficiently certain but the exact concentration must be determined by means of an appropriate solution of test substances.

It must be emphasized that the final decision about the nature of an analytical response is written into a report (Fig. 6), but this report is intended only for use as an information tool inside the laboratory. The report is part of the analyst's laboratory book keeping.

AUTOINTERPRET

The program INTERPRET was developed to support the analyst in interpreting and evaluating the large number of chromatograms that are produced during automated pesticide residue analysis. Within the last year the program was extended to a more automated version: AUTOINTERPRET. The aim was to transfer the integrator outputs from various gas chromatographs on-line to the master personal computer and to automate some parts of the described evaluation process. The final report should be of a quality similar to that created by personal interaction using the worksheet of INTERPRET. AUTOINTERPRET works in a similar way to INTERPRET, but it requires the setting of some parameters. Instead of the personal decision about the resemblance of retention times, a window must be set in which correspondence of retention times is accepted. As described under Methods, we apply with each of our gas chromatographic systems effluent splitting to at least two selective detectors. The ratio of response factors is an important measure of the similarity of a peak in the sample chromatogram to that of a calibrated pesticide. Pesticide peaks in food samples, however, may overlap with matrix compounds that contribute

NR	SAMPLE	FR	COUNTRY	DATE
1	RADISH	1	NETHERLANDS	1.9.87

PEAK	Rt (min)	PESTICIDE	Rt (min)	LIMIT (mg/kg)	FOOD	EST. CONC. (mg/kg)
5	28.464	ENDOSULFAN-I	28.470	0.200	for ROOT VEGETABLES	0.064
COMMENT: Confirmation for QUANTIFICATION required.						
8	31.781	ENDOSULFAN-II	31.797	0.200	for ROOT VEGETABLES	0.199
COMMENT: Confirmation for QUANTIFICATION required.						

Fig. 6. INTERPRET REPORT. Header: information about the analysed sample (number and name of the sample, clean-up fraction, origin, date of analysis). Report table: number and retention times of the evaluated peaks, name and retention times of the suspected pesticides, maximum tolerances for these pesticides in the analysed food, estimated concentration the pesticide would have if it contaminates the sample. Comment: decision about the next analysis step required for confirmation.

to the detector response and as a consequence change the response ratio. Therefore, a considerable deviation from the calibrated value of the response ratio may be observed even though the pesticide is present. To avoid false negative results, a relatively large deviation of the response ratio must be tolerated. As the nitrogen–phosphorus detector tends to vary considerably in its response values, the relative significance of its signals can be reduced according to the actual results obtained with test mixtures.

Finally, the analyst has the choice between two types of report. One summarizes all identified peaks and those which need additional analytical confirmation. This report is similar to that obtained with the personal interaction using INTERPRET. Additionally, it provides proposals about which of the installed gas chromatographic systems appears most suited for confirmation analysis. The other type of report contains the same information but additionally a list of all unidentified peaks.

Automated evaluation of sample chromatograms starts with recalibrating retention times and response values of the cataloged pesticides by reference to the actual data produced by a test mixture. After the extraction of a background chromatogram provided by the same type of food with identical origin and clean-up fraction from the catalog of matrix samples, every peak in the actual sample chromatogram is proved either to be a pesticide or a matrix compound by considering retention times, response values and clean-up information.

If only one pesticide resembles the sample peak in retention times and response values within the accepted windows, AUTOINTERPRET adds a confirmation table (Fig. 7, peak 5) with all available data for this pesticide to the report.

If two or more pesticides resemble the sample peak in retention times and response values within the accepted windows, AUTOINTERPRET adds a confirmation table (Fig. 7, peak 9) presenting gas chromatographic systems which appear most suited for confirmation analysis to the report. These systems are proposed on the basis of phase selectivity calculations. This means that the computer considers all compounds within a certain retention time window around the indicated pesticide and selects the system with the best resolution of all these compounds. These calculations also include the information available from response ratios.

Finally, the analyst must check which of the proposed confirmation steps is essential for the identification and quantification of those pesticides indicated by AUTOINTERPRET. This task is executed by means of the subprogram INTERPRET and results in the final report shown in Fig. 6.

RESULTS AND DISCUSSION

CAPA was designed for the analyst and developed by an analyst in the laboratory. The acceptance of any computer program by analysts depends on the effort required to learn it and on the speed with which results are obtained. Speed, however, is a very subjective criterion. When using computers it often means how quickly an answer to a frequently arising question is given. Therefore, the session starts with recalibration of all data in the main catalog with the results of the corresponding test mixture as actual references. This is the most time-consuming process and needs about 1 min. In this time all data are arranged in the computer's memory in a way that guarantees very rapid access from the interactive evaluation process. The com-

```
SAMPLE NUMBER =                    1
==================================

FOOD         COUNTRY       FR    DATE
-------------------------------------
RADISH       NETHERLANDS    1    1.9.87


PEAK 5:                    corrected retention time=  28.464 min

BEST FITTING SUBSTANCES: 1
DECISION:                  PESTICIDE
NEXT STEP:                 CONFIRMATION by means of other columns
                                        for analysing the sample.

********** C O N F I R M A T I O N  T A B L E **********

RETENTION TIMES

COLUMN     SAMPLE PEAK    ENDOSULFAN-I
-----------------------------------
A-SE54     28.464 min     28.470 min
---------------------
A-OV1701   32.71          32.727 min
A-SE30     _____          20.332 min



PEAK 9:                    corrected retention time=  32.941 min

BEST FITTING SUBSTANCES: 3
DECISION:                  PESTICIDE or MARTRIX COMPOUND
NEXT STEP:                 CONFIRMATION by means of other columns
                                        for analysing the sample.

********** C O N F I R M A T I O N  T A B L E **********

RETENTION TIMES

COLUMN     SAMPLE PEAK    DDT          Benodanil    MATRIXPEAK
-------------------------------------------------------------

A-SE54     32.941 min     32.951 min   32.898 min   32.938 min
---------------------
A-OV225    30.43          30.727 min   31.324 min   _________
A-SE30     _____          20.445 min   20.359 min   _________
```

Fig. 7. AUTOINTERPRET REPORT. Header: information about the analysed sample (number and name of the sample, clean-up fraction, origin, date of analysis). Report tables supplied by AUTOINTERPRET for sample peaks 5 and 9. The retention times resulting from the confirmatory analysis may be entered manually into the confirmation table directly in the laboratory as shown here. Comment: peak 5 was confirmed on an OV-1701 column, peak 9 was proven not to be DDT or benodanil by analysis on an OV-225 column. It is therefore considered to be a matrix peak.

puter loads in advance those data into the direct addressable memory which are most likely to be called up in the next evaluation step. For instance, when working with INTERPRET and scrolling through the peak table of the chromatogram being processed, in the background a pointer moves through the table of maximum tolerances to the pesticide which is recognized as that which most resembles the addressed sample peak. Simultaneously, the estimated concentration of the indicated pesticide is

calculated and all data about the suspected pesticide are extracted from the database and held in memory for direct access by means of function keys. For the user it seems as if the computer knows in advance what the next question will be.

During the last few months the program was tested by applying it to daily routine analysis. Although CAPA is complex, it proved to be easy to understand and to handle, because it follows strictly the analytical evaluation process. The piles of chromatograms, forms, listing and reference tables are eliminated by using a personal computer with a second monitor and our computer program.

CAPA seems to be a powerful tool for environmental analysis; nevertheless it is only one of the large number of software packages to be found in modern laboratories. Textwriters, calculators, statistical programs and spreadsheets are commonly used. Software for the control and management of analytical standards, such as BALANCE[7], are helpful supplements. Bidirectional data exchange and the transfer of reports between these programs and CAPA are essential for economic work and can be realized by applying standardized file formats.

Problems, however, are similar to those arising from the manual evaluation of chromatograms; it must be guaranteed that all data reflect the real and actual situations of the chromatographic systems in use. That means that regular updating of the data base is essential.

The interactive evaluation program INTERPRET is and remains the core of CAPA because it forces the analyst to make decisions using the original data. AUTOINTERPRET is intended as a crude filter to focus the analyst's attention in the morning or after a weekend to the samples analysed overnight that probably are contaminated. The proposals of how to achieve confirmation allow a rapid start in the morning with such confirmatory analyses. This gives the analyst the time for careful inspection of the other chromatograms of the screening analyses and the incoming confirmatory runs.

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