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MICROCOMPUTER PROGRAMMING IN BASIC FOR THE EVALUATION OF CAPILLARY GAS CHROMATOGRAPHY IN THE ANALYSIS OF PESTICIDE RESIDUES

I. MATRIXCOMP—A PROGRAM THAT FACILITATES THE RECOGNITION OF INTERFERING PEAKS FROM THE BIOLOGICAL MATRIX

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SUMMARY

Chromatograms of pesticide residues in food include peaks produced by pesticides and matrix compounds. Pesticide peaks are recognized by means of relative retention times and response factors; two detectors are used and internal standard methods are applied. Chromatograms of reference samples for all types of food are stored as raw data in a reduced format, together with tables of all chromatographic data for the matrix compounds. MATRIXCOMP provides the analyst with the chromatograms of the actual sample and the reference in parallel on a visual display screen for visual comparison. Simultaneously, the relevant chromatographic data for the sample, the reference and the calibration tables are displayed on a second screen page in a condensed form.

INTRODUCTION

In the analysis of pesticide residues in food, chromatograms include peaks produced by pesticides and peaks resulting from compounds from the biological matrix. The background chromatograms, representing the substances passing through the clean-up together with the pesticides, vary considerably with the variety of food analysed. Although the provenance might be different, background chromatograms produced by the same type of food show sufficient resemblance.

In this paper we describe a computer program designed to assist the analyst in evaluating the actual chromatogram. Chromatographic peaks from the biological matrix can be distinguished from those produced by pesticides simply by comparing the chromatogram of the actual sample with one of a food of the same type and similar origin, which was known to be free of pesticide contamination.

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METHODS

After a standardized clean-up[1], analysis of pesticide residues in food was performed by using a gas chromatograph (Sichromat 2, Siemens, Karlsruhe, F.R.G.), capillary columns, and effluent splitting to two selective detectors, an electron-capture detector and a flame photometric detector[2]. The signals from the detectors were transferred via an analog-to-digital converter to the microcomputer system (Trilab 2500, Trivector, Niederolm, F.R.G.), automatically processed by the manufacturer's software package, and stored as raw data and result files on a floppy disk.

Computer configuration

Our Trilab 2500 is a chromatographic data system, incorporating a visual display unit (VDU), 288 kbyte RAM, twin floppy disk drives (each diskette with 640 kbyte) and one 10 mbyte hard disk unit. The system includes a software package for evaluating all kinds of chromatographic data files and a BASIC interpreter.

Program

With the help of our program, MATRIXCOMP, actual chromatograms can be compared with the background chromatograms from foods of the same type and from the same region. These reference samples have been carefully checked to be free of residues of those pesticides, available as standards. In our laboratory a mass spectrometer is coupled to a gas chromatograph to enable us to detect amounts in the parts per billion range. The chromatograms of the reference samples are catalogued and stored on the hard disk unit in a reduced format. Identification of the pesticides that might contaminate the sample is performed by means of a table with retention times and response factors of nearly 200 substances.

The MATRIXCOMP program covers 32 kbyte and works with four internal memory files for the chromatographic raw data of the actual sample and reference sample, as well as for the corresponding result tables.

Program parts, generally used for automated processing of chromatographic data, are combined with subprograms designed to apply the analyst with tools for the visual comparison of the actual and reference sample on the visual display screen.

The analyst is conducted through the program by menus, which offer the following functions:

(1) Table of the chromatograms, stored on the hard disk, with name, variety, origin, and date of input;

(2) Table of the retention times and ratios of response factors for the actual sample;

(3) Corresponding table for the reference sample;

(4) Corresponding table for nearly 200 calibrated pesticides;

(5) The two chromatograms for the visual comparison are displayed in parallel;

(6) Expansion of critical parts of each chromatogram;

(7) Cursor-controlled call-up of chromatographic data of significance to the analyst;

(8) Manual input and actualization of the chromatographic data for the pesticides in the calibration table.

TABLE I

COMPILATION OF CHROMATOGRAPHIC DATA CALLED UP BY THE CURSOR, ACTIVATED IN THE SAMPLE CHROMATOGRAM

Abbreviations: RT = retention time; RRT = retention time relative to the internal standard aldrin; ECD = response relative to the internal standard aldrin; FPD = response relative to the internal standard O-2-naphthyldimethylthiophosphinate; ECD/FPD = ratio of the two response facors. Peaks with similar retention times. Retention time at the position of the cursor: 16.18.

	RT	*RRT*	*ECD*	*FPD*	*ECD/FPD*
Actual sample					
	16.18	0.9304	0.640	0.003	213.3
	16.34	0.9396	0.221	0	0
Reference sample					
	16.49	0.9396	0.094	0	0
Calibration table					
Metribucin		0.9197	0.642	2.788	0.231
Vinclozolin		0.9303	1.057	0.005	211.3
Alachlor		0.9448	0.120	0	0

A special help-function offers the analyst a list of the available orders with a short explanation of their functions. The handling of all numerical and graphical data is very convenient, because the analyst has a choice between three screen pages. All outputs can be examined on the screen or may be printed with a plotter.

A normal raw-data file consists of 3000 to 4000 points, representing a chromatogram of 30 to 40 min. This high resolution is necessary for the accurate calculation of peak areas, for baseline corrections, and other manipulation routines. Reference chromatograms destined for the visual comparison on the screen can usually be catalogued as 1000 data points. This reduction minimizes the memory space necessary for the chromatogram library on the hard disk. Another aspect is that the screen resolution in the horizontal direction is limited to 1000 points. Therefore, the reduction does not influence the visual information supplied on the screen for comparing chromatograms.

RESULTS

How the program is used was demonstrated by applying it to an analysis of pesticide residues in a real food sample. The cleaned sample was injected into the gas chromatograph and the effluent was split to the two selective detectors. The signals were recorded in parallel and processed by applying the "Trilab" software. By means of the calibration table, small amounts of vinclozolin and procymidone were identified at retention times of 16.18 and 19.30 min in the actual sample (indicated by arrows in Fig. 1). In the MATRIXCOMP program the corresponding electron-capture chromatogram of a reference sample was searched and loaded from the hard disk. The two chromatograms were displayed together on the screen (Fig. 1).

The lower half shows a chromatogram of an actual sample of strawberries from Italy: the upper half the corresponding reference. The two chromatograms show

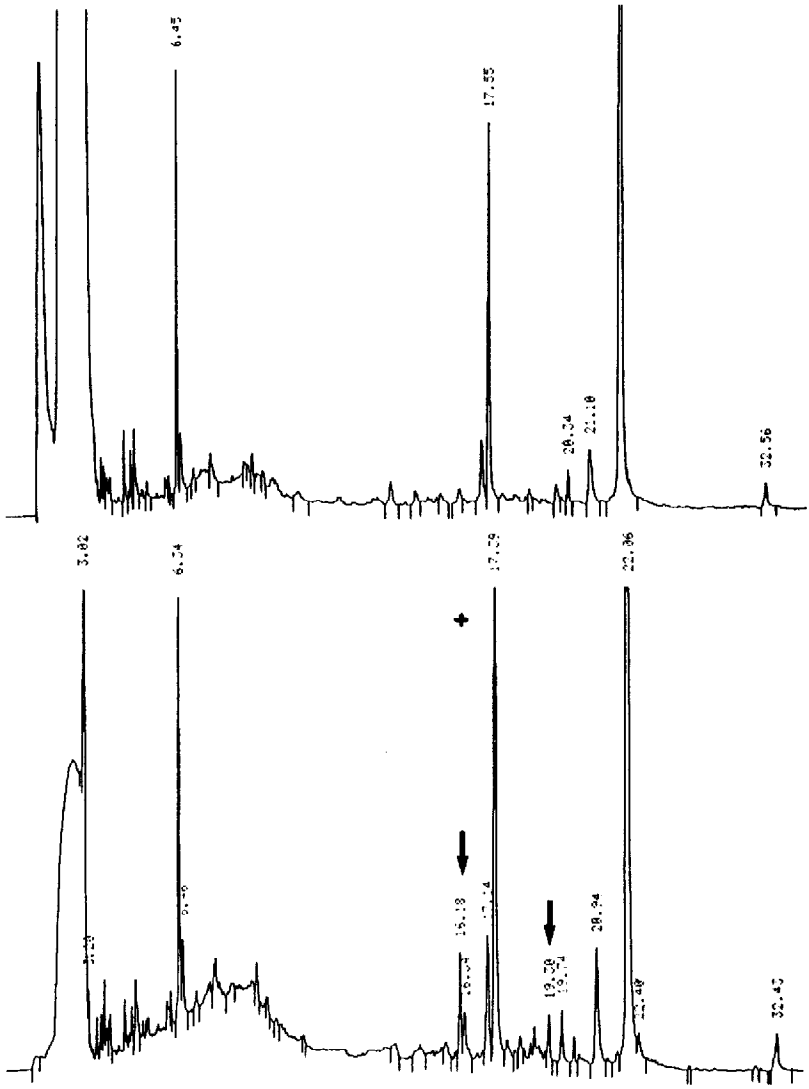

Fig. 1. Electron-capture chromatograms from strawberries from Italy. Top, reference sample; bottom, actual sample with activated cursor and two peaks from pesticides, indicated by arrows.

a characteristic resemblance in their pattern of the major peaks. Two of them are plasticizers, which are typical contaminants in pesticide residue analysis. The peak at a retention time of 6.34 min as well as the smaller peak at 32.43 min are permanent contaminants in our chemicals. The internal standard aldrin appears at 17.39 min with a smaller satellite at 17.14 min.

These four peaks were found in all our analyses and form a typical background frame for all chromatograms. The largest peak in both chromatograms is another plasticizer, which contaminates all packed strawberries from Italy this year. In ad-

dition to this significant peak pattern, a number of smaller peaks, similar in retention time and appearance, can be found in both chromatograms.

By means of the subprogram "cursor", a small cross (Fig. 1) is activated. It can be moved all over the screen by pressing the cursor keys. The cross is used to indicate individual peaks. By pressing the return key the data listed in Table I are displayed on the second screen page. Simultaneously, this information is prepared for peaks in a specified retention window for the reference sample and for all calibrated pesticides in the same range.

Provided with the relevant information in a very condensed format, the analyst must decide whether the indicated peak is produced by a calibrated pesticide, an unknown matrix compound, a common environmental contaminant or perhaps an unexpected pesticide. The confirmatory procedure for calibrated pesticides by use of effluent splitting and two-dimensional capillary GC was described elsewhere[2–4]. If an unknown pesticide cannot be ruled out, gas chromatography–mass spectrometry must be used for identification. An additional tool for handling chromatograms is the expansion procedure, which enables the analyst to study selected parts of the chromatogram in more detail.

DISCUSSION

Multi-residue pesticide analysis in a whole range of foods is performed by standardized extraction and clean-up procedures. In most laboratories the vast majority of samples is divided into just two groups: food samples with low fat content and food samples with high fat content. This means that the clean-up procedures must remove a variety of matrix compounds in nearly 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 GC. It is surprising to what a great extent the clean-up procedures now in use in connection with selective detection in GC fulfil this requirement. However, several peaks produced by matrix compounds are found in all chromatograms.

The aim of our MATRIXCOMP program is to facilitate the recognition of such interfering peaks in screening for pesticide residues. The evaluation follows the same line as that used in routine analysis, where experienced analysts collect data on interfering substances in the biological matrix in order to avoid wasting their time in hunting chimeras. The advantage of our program is that the information is as complete as possible. Not only retention times, but the entire background chromatograms from the two detectors and all interesting chromatographic data are available for the evaluation of actual chromatograms.

Although the MATRIXCOMP program was developed for pesticide analysis in food, it also might be useful for other environmental samples, the determination of the provenance of mineral oil or standardization in quality control.

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