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ORGANIC MICROPOLLUTANTS IN AIR AND WATER

SAMPLING, GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC ANALYSIS AND COMPUTER IDENTIFICATION

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SUMMARY

Organic micropollutants are sampled by dynamic enrichment on a porous polymer column and subsequently thermally eluted in a flow of helium. The eluted compounds enter gas chromatograph inlet and then pass into two parallel glass capillary columns with different stationary phases, in which they are separated. The separated compounds are detected by gas chromatographic (GC) detectors and by a mass spectrometer that is connected to one or other of the two capillary columns by "heart cutting" systems. The GC and mass spectrometric (MS) signals are fed via interfaces into a minicomputer which controls the MS scan and performs data acquisition, reduction and treatment on-line and off-line.

The resulting GC and MS data are displayed on a line printer or a visual display unit. The minicomputer is connected by a telephone line to an IBM 370/165 computer, where a library search system has been implemented.

Some difficulties encountered, data on the sampling recovery of model compounds and the identification of compounds in air and water samples by GC–MS data and library searches are discussed.

INTRODUCTION

Within the framework of the Environmental Programme of the Joint Research Centre of the European Economic Community, we are developing[1] an analytical unit for the analysis and identification of organic micropollutants in air and water samples.

The commonest earlier approach to the analysis of organic pollutants in environmental samples was the determination of some pre-selected compounds that had previously, often by chance, been recognized as harmful (*e.g.*, pesticides and carginogens) but neglecting many other compounds arbitrarily, simply because of their unknown identities.

In recent years, the gradual discovery of a wide variety of compounds in the

environment (*e.g.*, gasoline and chlorinated hydrocarbons in various types of water) called for a new approach, starting with the assumption that the nature of most detectable pollutants is unknown initially and that they should therefore be identified as certainly as possible before necessarily being shown to be potentially harmful.

Both the laboratories of the Environmental Protection Agency in the U.S.A.[2], and the European laboratories involved in the EEC–COST Project 64b[3], for instance, are working along these lines.

The method of choice is to couple different techniques, comprising a sampling procedure, gas chromatographic (GC) separation and mass spectrometric (MS) detection. The large amount of data produced by such an analytical unit has to be handled and evaluated by a computer, which, in addition to reducing and combining the data, is able to identify (by library searches) compounds for which reference data exist or to give structure approximations for those compounds for which no reference data are available.

At present, these analytical units are suitable only for organic compounds that are amenable to GC separation, *e.g.*, compounds with not too high a boiling point and good thermal stability. This factor, of course, limits the range of compounds that can be analyzed in a sample and, in some respects, simplifies the analytical profile of the sample itself, which may contain compounds that do not pass the GC separation step. As stated by Grob *et al.*[4], "Present knowledge about organic substances, mostly in water, is biased as analytical research is not directed by what is in the water or by what we want to find out but by what we are able to find out by using the available methods".

However, GC still remains the method of choice because of its outstanding separating power. High-pressure liquid chromatography, when its separation efficiency has been increased, could become an alternative separation method for polar, high-boiling and thermally unstable compounds, and work is in progress to assess the possibilities of linking such a technique with MS.

DESCRIPTION OF THE UNIT

Fig. 1 gives a flow scheme of the unit. Organic micropollutants are sampled by dynamic enrichment on a porous polymer glass adsorption column and afterwards thermally eluted with a flow of helium. The eluted compounds enter, via a GC inlet, two parallel glass capillary columns (0.3 mm I.D.; 60 m length; Varian Model 2700)

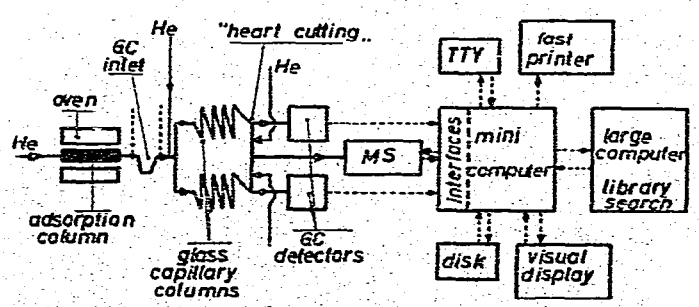

Fig. 1. Flow scheme of analytical unit.

with different stationary phases, in which the compounds are separated. The separated compounds are detected by flame-ionization detectors (FIDs) and a mass spectrometer (quadrupole type, Riber Model QML 51; mass range 4–600; resolution $m/\Delta m$ = 600; detectability 10^{-9}–10^{-12} g/sec), which is connected to one or other of the two capillary columns by "heart cutting" systems. The GC and MS signals are fed via interfaces into a minicomputer (General Automation SPC-16/65; 16-bit words; 16K core memory; CPU cycle time 960 nsec) which controls the MS scan and performs data acquisition, reduction and treatment on-line and off-line, in this instance using a supplementary disk memory of 2.5 megawords. The minicomputer is controlled by a teletype or a visual display unit (VDU) (Tektronix 4010-1) and the GC–MS data are displayed either on the VDU or on a line printer (Centronics 101, 132 columns at 165 characters/sec). The minicomputer is linked by a telephone line to an IBM 370/165 computer, where a library search based on the method developed by Naegeli and Clerc[5] has been implemented. A data base of 30,000 mass spectra based on the MSDC and Wiley collections of spectra is available.

SAMPLING AND ELUTION

Air

In a previous paper[6], we described the sampling of organic air pollutants by dynamic enrichment on an adsorption column. This technique was judged to be sound by many other workers[7–16] because: (a) the adsorbed compounds can be thermally eluted, thus avoiding the need for ultra-pure solvents; (b) the adsorption and desorption procedures can be easily automated; (c) the dynamic enrichment allows both complete adsorption of substances that have a retention volume lower than the sample volume passing through the adsorption column and, for more volatile compounds, an equilibrium concentration proportional to the concentration in the original sample; and (d) the sampling can be performed *in situ*.

From the various adsorbents available, a porous polymer, Tenax GC[17] (poly-*p*-2,6-diphenylphenyleneoxide, surface area *ca.* 30 m²/g, 60–80 mesh, manufactured by AKZO, Arnhem, The Netherlands), was chosen because it is hydrophobic, has a low adsorption strength, allowing the thermal elution of relatively high-boiling compounds (*e.g.*, terphenyls), has a good thermal stability and does not react with most organic pollutants.

A glass column (*ca.* 15 cm length, 1 cm I.D.) filled with 2.5 g of Tenax was adopted. The column is pre-conditioned at 350° for 3 h and subsequently at 200° overnight under a flow of high-purity helium. The air sample (2–40 l, according to the contamination level) is aspirated *in situ* into the porous polymer adsorption column (Fig. 2) by a pump at a speed of 0.5 l/min. After sampling, the column is closed at both ends and taken to the laboratory for elution and analysis.

Water

In contrast to air, for which adsorption seems to be the most promising sampling technique, many other sampling procedures have been envisaged for water, *e.g.*, distillation, freeze-drying, liquid–solid adsorption, headspace analysis, gas-phase stripping, and batchwise and continuous liquid–liquid extraction. The relative merits and drawbacks of many of these techniques have recently been discussed by several

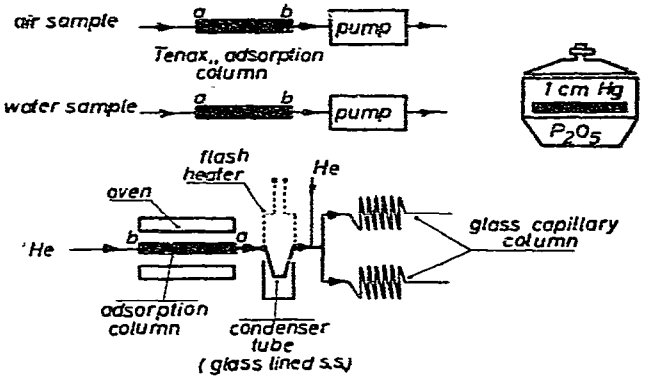

Fig. 2. Flow scheme of sampling and elution system.

workers, particularly Mieure and Dietrich[18], Grob[19] and Bertsch *et al.*[20], who indicated that liquid–solid adsorption on porous polymers or gas stripping followed by absorption on charcoal or porous polymers, with subsequent thermal or solvent elution, is very suitable for the sampling of organic substances in waters. The gas-stripping technique has been applied by several workers[20–22] and a closed loop system has been used by Grob *et al.*[4]. Liquid–solid adsorption on polymers has been adopted by several others[23–27].

For water, we use the same system as for air (Fig. 2). After several experiments, we increased the dimensions of the sampling column to contain *ca.* 4 g of Tenax mixed with 20% of 60–80-mesh glass beads in order to facilitate the flow of water and to prevent cracks in the column bed during the elution (heating) process. These cracks must not be present, otherwise preferential routes are formed and the water sampled is not able to come into contact with the entire polymer bed, resulting in poor recoveries. Normally, 0.5–1.5 l of water are sampled, depending on the contamination level. Water is aspirated *in situ* into the porous polymer adsorption column by a peristaltic pump at 5–7 ml/min.

After water sampling, the column must be dried so as to prevent the residual interstitial water from disturbing the GC–MS operation. The best procedure, which does not cause severe losses of compounds, is to leave the column overnight in a desiccator containing phosphorus pentoxide at 10 mmHg pressure.

Elution

For both air and water, the elution of the adsorption columns is carried out thermally in a sense opposite to that of the sampling (Fig. 2, b→a) with a flow of helium of *ca.* 15 ml/min. During the elution at 270° (20 min for air and 40 min for water), the eluted compounds are trapped in a glass-lined stainless-steel U-tube (1/16 in. for air, 1/8 in. for water) at −180°. When the elution is completed, they are flash-heated into the two GC glass capillary columns. The flash temperature of 300° is reached in 15–20 sec. Fig. 3 shows the actual configuration of the elution system.

Recovery

Tables I and II give some recoveries for model compounds in air and water.

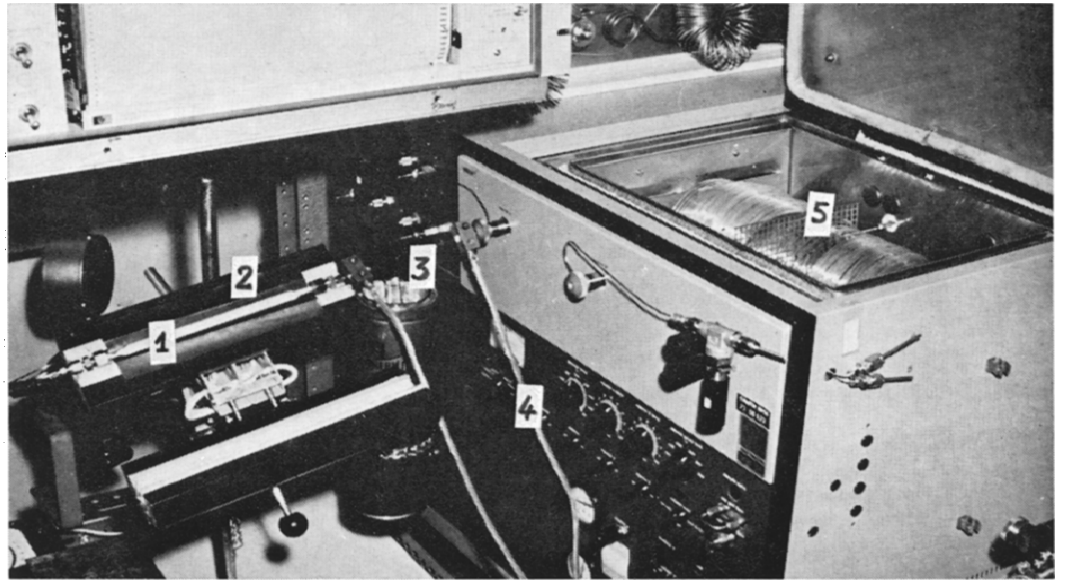

Fig. 3. Actual configuration of elution system. 1 = Tenax column; 2 = oven; 3 = U-tube condenser; 4 = flash heater cables; 5 = dual-column gas chromatograph.

TABLE I

RECOVERY OF MODEL ORGANIC POLLUTANT COMPOUNDS FROM AIR

Compounds adsorbed on Tenax at 20° and desorbed at 250–270° under a flow of helium.

Compound	*Recovery (%)* *
n-Hexane	100
Light petroleum (b.p. 80–100°)	90
Light petroleum (b.p. 100–120°)	92
Diphenyl	96
Acetone	97
Diphenylamine	93
o-Cresol	90

* Mean relative standard deviation: 5% at the ppb level.

In air, the recovery for compounds as volatile as *n*-hexane is 100% provided that the retention volume of this compound at 20° (about 30 l) is not exceeded. Compounds of different polarity can easily be adsorbed and eluted from Tenax with a mean relative standard deviation of about 5% at the ppb* level.

In water, the recoveries of compounds that are very soluble, such as pyridine and phenol, are poor. Tests were made with spiked water, prepared by dissolving the model compounds in methanol and adding them to water that had been purified by passing it through a Tenax column.

The recovery tests were normally performed at a pH value near to neutrality;

* Throughout this article the American billion (10^9) is meant.

TABLE II

RECOVERY OF MODEL ORGANIC POLLUTANT COMPOUNDS FROM WATER

Compounds adsorbed at 20° by passing water directly through Tenax and desorbed at 250–270° under a flow of helium.

Compound	*Added (ppb)*	*Mean recovery (%)*	*Relative standard deviation (%)*
Benzene	22.5	99	30
Pyridine	48.7	41	3
n-C_{11}	14.2	70	5
Aniline	30.5	89	8
Phenol	19.8	45	14
p-Cresol	19.9	89	6

other experiments carried out at acidic or basic pH values did not substantially improve the recoveries. In order to increase the recovery for water-soluble compounds, one could envisage the use of two Tenax columns in series. Benzene, in spite of a good mean recovery, has a comparatively high relative standard deviation; during the long drying of the column in the desiccator, some losses of the more volatile compounds might occur.

SEPARATION

The analysis of complex mixtures of organic pollutants in air and water requires a high-resolution separation system[4,19]. Glass capillary columns meet this requirement for several reasons: (a) they have a good separation power, (b) they allow the elution of relatively high-boiling compounds at relatively low temperatures, (c) the amount of material they can handle is in the range obtained by most of the actual sampling–enrichment systems and (d) the carrier gas flow-rates (2–4 ml/min) are compatible with the pumping capacity of most of the presently available mass spectrometers for a direct GC–MS connection.

Two columns in parallel are employed, with different stationary phases (normally OV-101 and OV-225 or Silar 10C) in order to evaluate the Kováts retention indices (ΔI) for the GC identification of compound classes. The ΔI values are normally compared with reference values obtained on the same stationary liquids on a separate GC system[28].

The glass capillary columns were drawn from soda-glass tubing of 8 mm O.D. and 3 mm I.D. using a glass-drawing machine. Normally columns of 60 m length and 0.3 mm I.D. are used.

Several procedures and materials are used for column pre-treatment: etching with hydrochloric acid[29–31], silanization[32], surfactants[33,34], deposition of particles such as Silanox 101[35] and Carbowax[36,37]. Similarly, for column filling dynamic and static methods are used. We obtained the best performance using the following conditions.

For OV-101 columns, the soda-glass capillaries are washed with dichloromethane and treated three times with a 1% solution of benzyltriphenylphosphonium chloride (BTPPC) in dichloromethane. After drying, a 20% solution of OV-101 in *n*-octane is

flushed through at *ca.* 40 cm/min. A column prepared in this manner is good for eluting hydrocarbons, basic compounds such as aniline and dimethylaniline and weakly acidic compounds such as dimethylphenols and alcohols. However, strongly acidic compounds such as phenols and chlorophenols are eluted with some tailing. The use of Carbowax 20M instead of BTPPC did not improve the elution of these latter compounds.

For OV-225 or Silar 10C columns, the soda-glass capillaries are etched at 500° for 2½ h with gaseous hydrogen chloride. After etching, the residual hydrogen chloride is removed with dry nitrogen and the columns are sealed until they are to be coated. A 10% solution of the stationary phase in dichloromethane or chloroform is passed through the column (40 cm/min).

These simple procedures are reproducible, and although they do not give optimal columns, they represent a good compromise for our purposes. A 60-m column normally exhibits a separation number* of 30–40 relative to C_{13}–C_{14} hydrocarbons.

GC–MS COUPLING

As the carrier gas flow-rate in the glass capillary columns used (*ca.* 4 ml/min) can be managed easily by the pumping system of the MS, direct GC–MS coupling was decided upon. Moreover, it was considered desirable to have (a) at the end of each column, a splitter to an FID in order to control the eluted compounds with a sensitivity higher than that of a normal total ion current monitor and to facilitate quantitative measurements, and (b) the two columns connected alternatively and on-line to the mass spectrometer. The scheme adopted is shown in Fig. 4.

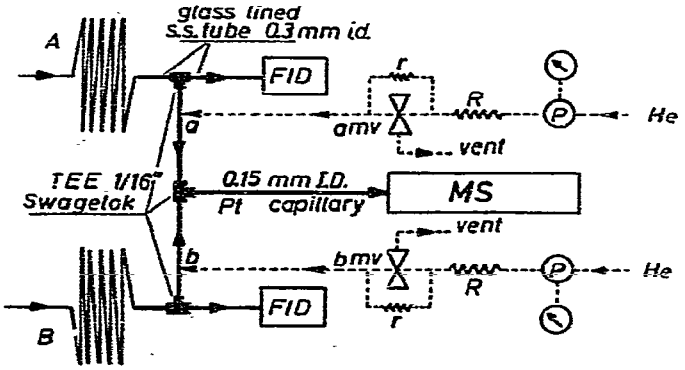

Fig. 4. GC–MS "heart cutting" connection.

The mass spectrometer is connected to the GC columns by a platinum capillary tube (0.15 mm I.D., *ca.* 50 cm length), allowing a flow-rate of 3–4 ml/min. Compounds leaving columns A and B always enter the GC detectors, whereas whether or not they enter the mass spectrometer depends on the "heart cutting" conditions, *i.e.*, the helium flow-rates in a and b. These flow conditions are regulated by two electromagnetic valves (amv, bmv) and the restrictors r. With an appropriate helium

* The separation number is the number of peaks completely separated between a pair of consecutive hydrocarbon homologues.

flow-rate in a (amv open) and a very small flow-rate in b (through r, bmv closed), compounds eluted from column A enter the FID only, while compounds eluted from column B enter both the FID and mass spectrometer, and *vice versa*. About 50% of the products emerging from the GC columns enter the mass spectrometer. The entire system was constructed using glass-lined stainless-steel tubes with an I.D. of 0.3 mm. The joints were soldered in order to reduce diffusion of air into the system. Owing to its rapid response, the system is also ideally suited to preventing solvent peaks from entering the mass spectrometer in the case of normal GC injection.

DATA ACQUISITION AND TREATMENT

GC and MS data acquisition, as well as the MS scan, are controlled by the GA SPC 16/65 minicomputer[38]. A commencement dialogue permits one of three operation modes (GC, MS, GC–MS) to be selected and to change or save previously established experimental parameters. The MS scan takes *ca.* 27, 13 or 9 samples per mass unit instead of jumping from peak maximum to peak maximum. The latter method tends to introduce major intensity variations owing to changes in peak shape at the relatively high MS working pressure during GC–MS operation.

In order to save minicomputer time, an interface (PEGASO), constructed by our Electronics Division[39], digitally smoothes the MS ion current signals and detects peak maxima. Thus, sufficient computer time is available to reduce on-line data from up to 4 GC channels (sampling rate 20 Hz per channel) during MS operation. Mass spectra are continuously taken at a scan rate of 600 a.m.u./sec during GC peak elution, and at variable intervals otherwise (every 5–15 sec). This can be done without loss of information, as the mass spectrometer is less sensitive than the FID, unless it is operated in the mass chromatogram mode, when it is run continuously.

The GC data are reduced on-line. For each peak, its number, the elution time and height of the start, inflexion, maximum and end-points, the first derivative at the inflexion points, and the front and back half-areas are calculated on-line and stored on disk. The separation of fused peaks, the choice of the separation algorithm (perpendicular drop, tangent), the baseline correction, the determination of corrected peak area and the calculation of Kováts retention indices are performed off-line. An analysis report is output on the line printer.

Mass spectra are stored directly on a disk and processed off-line. More than 3000 spectra can be stored for a single GC–MS run. Processing is display-oriented. With simple commands, reconstructed gas or mass chromatograms are generated. By means of the cursor on the VDU, they can be expanded and spectra at interesting points, together with related background spectra, can be selected. Single or averaged background spectra can be subtracted.

All data acquisition and processing software has been appropriately developed, is very flexible and can easily be adapted to new problems.

DATA INTERPRETATION SOFTWARE

Currently, only library search techniques[5,40–43] offer a reasonable chance of automatically identifying spectra or compounds originating from as large a number of different classes as do environmental organic pollutants. Other approaches, such

as classification techniques[44–46] or heuristic interpretation algorithms[47], are either not sufficiently conclusive or are practicable only if applied to the interpretation of spectra belonging to a single, well defined compound class.

While on the one hand, the identification probability increases with the size of the reference library, on the other hand the computer time involved and hence the cost also increase. For this reason, it was decided to split the MS interpretation into two steps. In the first step, currently occurring pollutants (at present mainly hydrocarbons) are identified with the reverse search technique proposed by Abramson[48]. A small reference library of spectra of these compounds, all of which have been measured with the unit's quadrupole mass spectrometer, is matched against the spectra

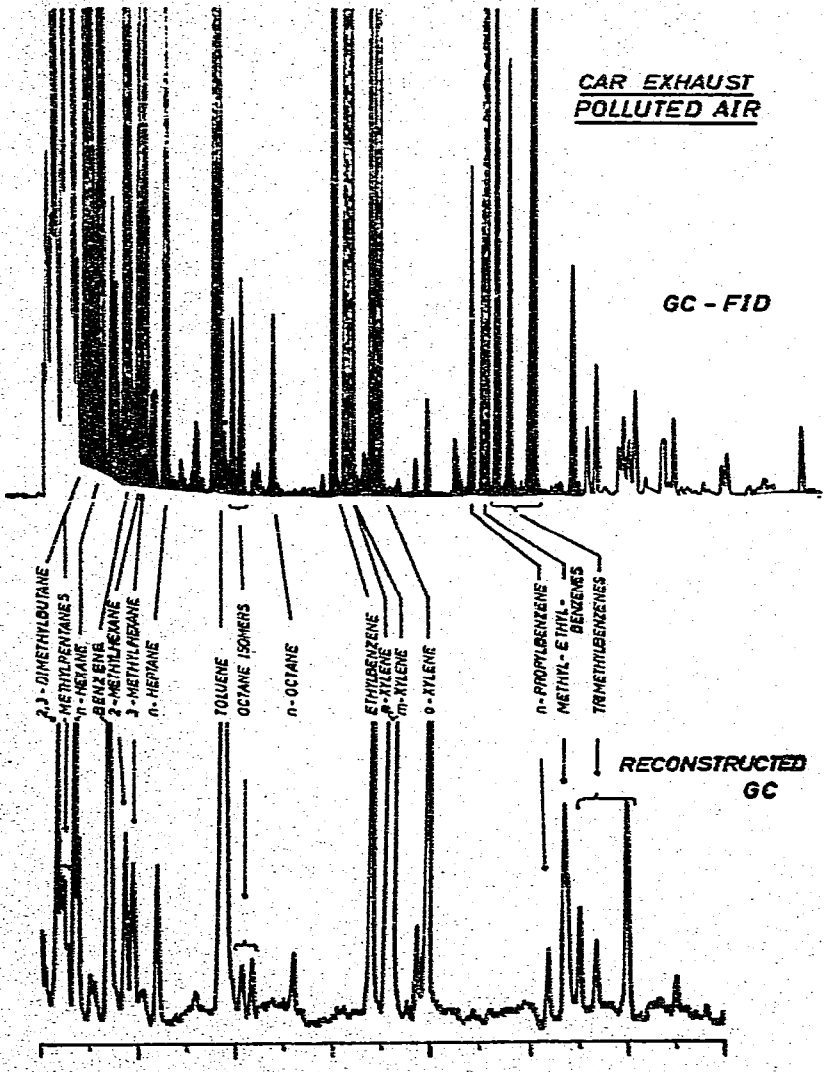

Fig. 5. FID (upper) and reconstructed chromatogram of an air sample polluted with car exhaust fumes.

taken during a GC–MS run. A report is given on the line printer containing GC peak numbers in increasing order, the numbers of those associated mass spectra for which one (or several) hit(s) has been found, the identified compound names, the respective Kováts retention indices and the similarity factors. This job is run entirely on the minicomputer.

Fig. 5 shows an FID chromatogram (above) and the corresponding reconstructed chromatogram (below) of a car exhaust polluted air sample. The names indicated were assigned by use of the reverse search library.

The interpretation of the mass spectra of GC peaks not identified by the reverse search is effected in a second step, for which the Clerc library search algorithm[5,49] was adopted. This algorithm was designed particularly to find similarly structured compounds, even if the spectrum of an unknown compound itself is not available in the library. Mass spectral features rather than original mass spectra are compared with a feature library derived from the MSDC[50] and, recently, the Wiley[51] collections of spectra. The sum of the features of a spectrum is called a signature. Features are coded in one bit, *i.e.*, they are either present or absent. Signatures of unknown spectra are generated by the minicomputer and, up to 20 at a time, transferred to our calculation centre, where the search algorithm and the library are implemented on an IBM 370/165 computer. The resulting hit lists of the ten best fits are output on the line printer.

Fig. 6 shows two search results, which were obtained with the MSDC library only. The upper set (a) is the hit list of a compound that is obviously a C_2-substituted

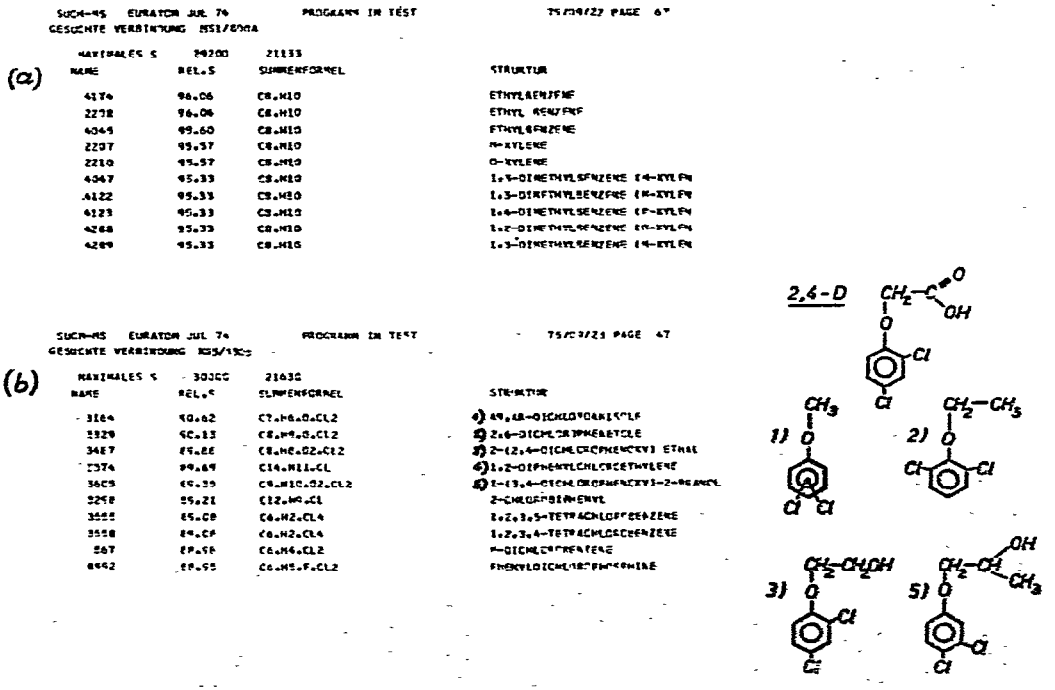

Fig. 6. Printouts of MS identification library search.

benzene. Owing to the similarity of the different isomer spectra, the assignment of ethylbenzene as the correct answer was made on the basis of GC retention data. This example is one of our early attempts and the ethylbenzene spectrum is now included in the reverse search library. Fig. 6b reports a less evident example. A match of the unknown compound against the entire MSDC library resulted in a completely non-significant hit list with very different and complex compounds, *ar*,*ar*-dichloroanisole being in the last position. As a chlorine pattern classifier gave clear evidence for the presence of chlorine in the unknown compound, a second match against the sub-library of only chlorine-containing compounds was made and gave the result shown Fig. 6b. In spite of the relatively bad match factors, four of the first five hits have a dichlorobenzoxymethyl group in common, which was useful evidence in identifying the unknown compound as the pesticide 2,4-D.

The last example shows that pre-classification of an unknown spectrum[45] may be useful not only in saving computer time by reducing the library to be matched, but also by increasing the structure elucidation power of a search result, especially when only relatively poor similarity indices are obtained. The application of further classifiers is being explored.

The identification of unknown structures by a library search may be complicated if the names of the hit list members, which are often trivial, do not indicate related structures. This difficulty can be circumvented if the reference data file contains a structure code, such as the Wiswesser Line Notation (WLN), which is available for the Wiley registry.

Within the framework of a data bank for environmental chemicals (a description of this data bank, ECDIN, is given in refs. 52 and 53), the Crossbow[54] program developed by ICI was implemented on our IBM 370/165 computer. Via teleprocessing, it generates, from the WLN, semi-structural formulae that can be displayed either on the line printer or on the VDU. Using this option, sub-libraries of selected compound classes required in connection with the classification of unknown spectra can easily be generated. The structural fragment option also offers an additional criterion, apart from similarity indices, for the assessment of a search result. As illustrated in Fig. 6b, a structural fragment or a combination of such fragments that is common to several members of a hit list can more reliably be supposed to be present in the unknown compound. This option also needs further exploration.

PRACTICAL APPLICATIONS

Fig. 7 shows the effectiveness of the sampling of air on Tenax. Chromatogram B is the result of the sampling of 2 l of air from near a car parking area on Tenax, and chromatogram C of the sampling of 40 l of air in a woody area far from direct contamination by car exhaust fumes. Both samples were taken in winter. By comparison of chromatograms B and C with chromatogram A, which represents a standard mixture of gasoline plus diesel oil, it follows that both air samples are polluted by little except gasoline[9,13,14]. The larger sampling volume of 40 l for the sample from the woody area accounts for the higher proportion of high-boiling materials in chromatogram C than in A. The peaks numbered in chromatogram A, which were also identified in chromatograms B and C, are listed in Table III.

Fig. 8 represents the chromatogram of an air sample of 40 l taken in a woody

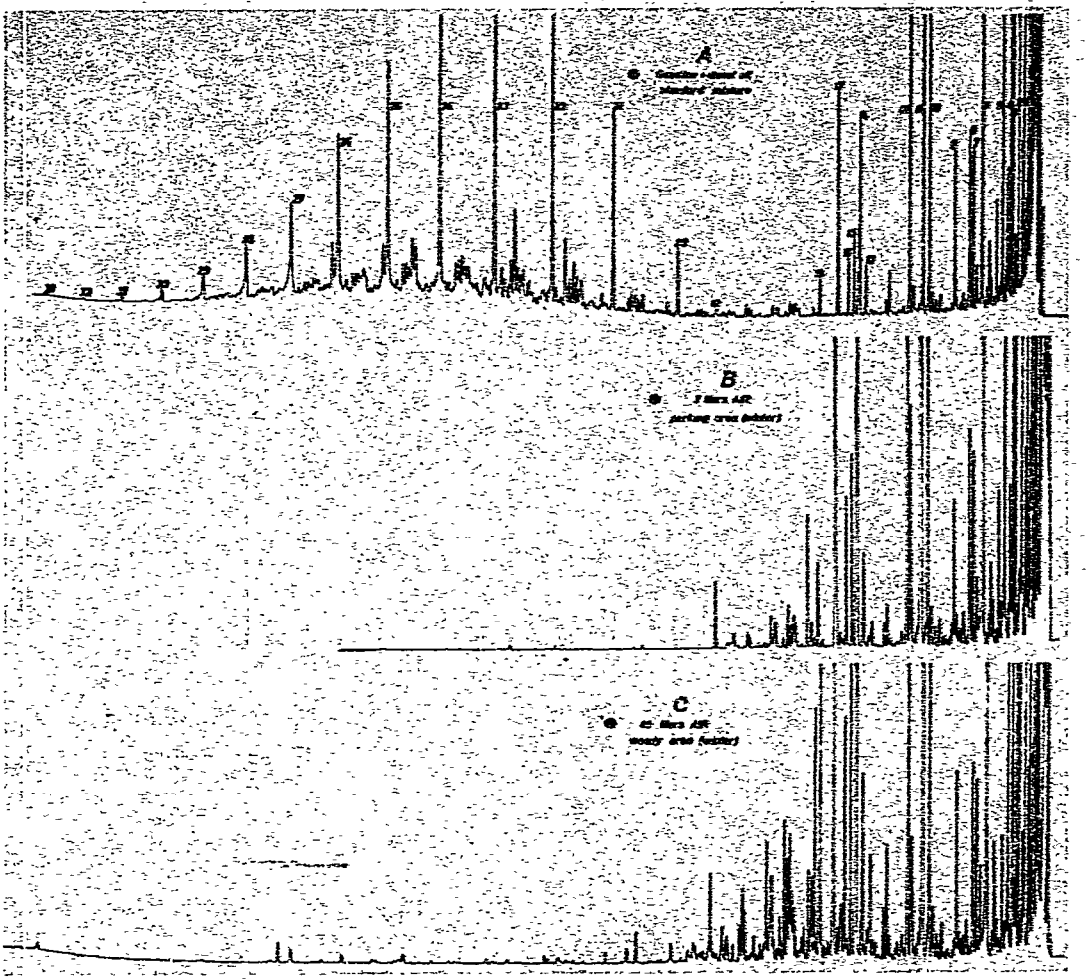

Fig. 7. Profiles of organic volatiles in air. (A), Standard mixture of gasoline plus diesel oil; the numbered peaks are those in Table III; (B), 2 l of air from a car parking area (winter); (C), 40 l of air from a woody area (winter). Glass capillary column, 60 m × 0.3 mm I.D., OV-101. Helium flow-rate *ca.* 4 ml/min. Temperature programme: 40° for 5 min, 40 to 250° at 2°/min. Detector: FID, 270°.

area during the summer. The numbered peaks are those listed in Table III, and again the air appears to be polluted mostly by gasoline. Nevertheless, the chromatogram contains some differences compared with that for the winter sample (Fig. 7, chromatogram C): a smaller proportion of light compounds and some unknown peaks marked with an asterisk, probably belonging to the hydrocarbon emissions from the trees. The identification of these compounds is in progress.

Fig. 9 shows the effectiveness of water sampling. Chromatogram A is the result of the sampling on Tenax of 1 l of tap water spiked with 10 ppb of gasoline plus 10 ppb of diesel oil. By comparison of this chromatogram with chromatogram B and with chromatogram A in Fig. 7, it is easy to distinguish the "fingerprint" of the

TABLE III

IDENTIFICATION OF COMPOUNDS

Peak numbers refer to chromatogram A in Fig. 7.

Peak number	*Compound*	*Peak number*	*Compound*
1	*n*-Hexane	18	*n*-Decane
2	Benzene	19	Naphthalene
3	2-Methylhexane	20	*n*-Dodecane
4	3-Methylhexane	21	*n*-C_{13}
5	*n*-Heptane	22	*n*-C_{14}
6	Toluene	23	*n*-C_{15}
7	Octane isomer	24	*n*-C_{16}
8	Octane isomer	25	*n*-C_{17}
9	*n*-Octane	26	*n*-C_{18}
10	Ethylbenzene	27	*n*-C_{19}
11	*m*-Xylene + *p*-xylene	28	*n*-C_{20}
12	*o*-Xylene	29	*n*-C_{21}
13	*n*-Propylbenzene	30	*n*-C_{22}
14	Methylethylbenzenes	31	*n*-C_{23}
15	Trimethylbenzene	32	*n*-C_{24}
16	Trimethylbenzene	33	*n*-C_{25}
17	Trimethylbenzene		

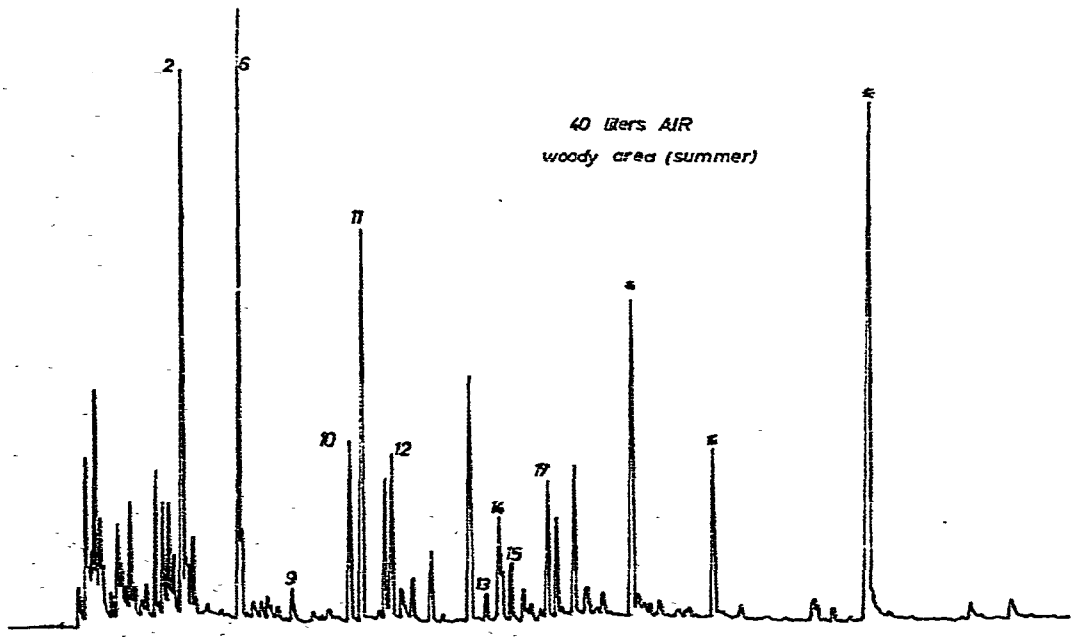

Fig. 8. Profile of organic volatile compounds in air; 40 l of air from a woody area in summer. Numbered peaks are those in Table III; peaks with asterisks are unknown compounds. Chromatographic conditions as in Fig. 7. Only the portion of the chromatogram relative to the gasoline range is shown.

gasoline and diesel oil superimposed on the "fingerprint" of the tap water. The numbered peaks refer to those listed in Table III. Chromatograms B and C show the organic compounds present in 1 l of tap water and in 1 l of Lake Maggiore surface water. The two chromatograms appear similar and in fact Lake Maggiore is used as a source for this tap water. Comparison of B and C with A makes it evident that both contain compounds present in gasoline[55] (marked with asterisks). Contrary to reports by some workers[22], it does not seem that tap water, in spite of the chlorination process, contains more compounds than the precursor. This is probabiy due to the mild chlorination process used, which, performed at a pH value of *ca.* 8, does not cause easy incorporation of chlorine into the aromatic compounds (*e.g.*, those belonging to the gasoline type)[56].

Chromatograms D and E show the organic compounds present in 1 l of bottled mineral waters from two different sources. Both samples appear "clean" and contain, surprisingly, similar peaks. A possible explanation could be that these compounds belong to the plastic tubing used in the bottle filling system or to the plastic liners of the stoppers, the last large peak having in fact been identified as a phthalate.

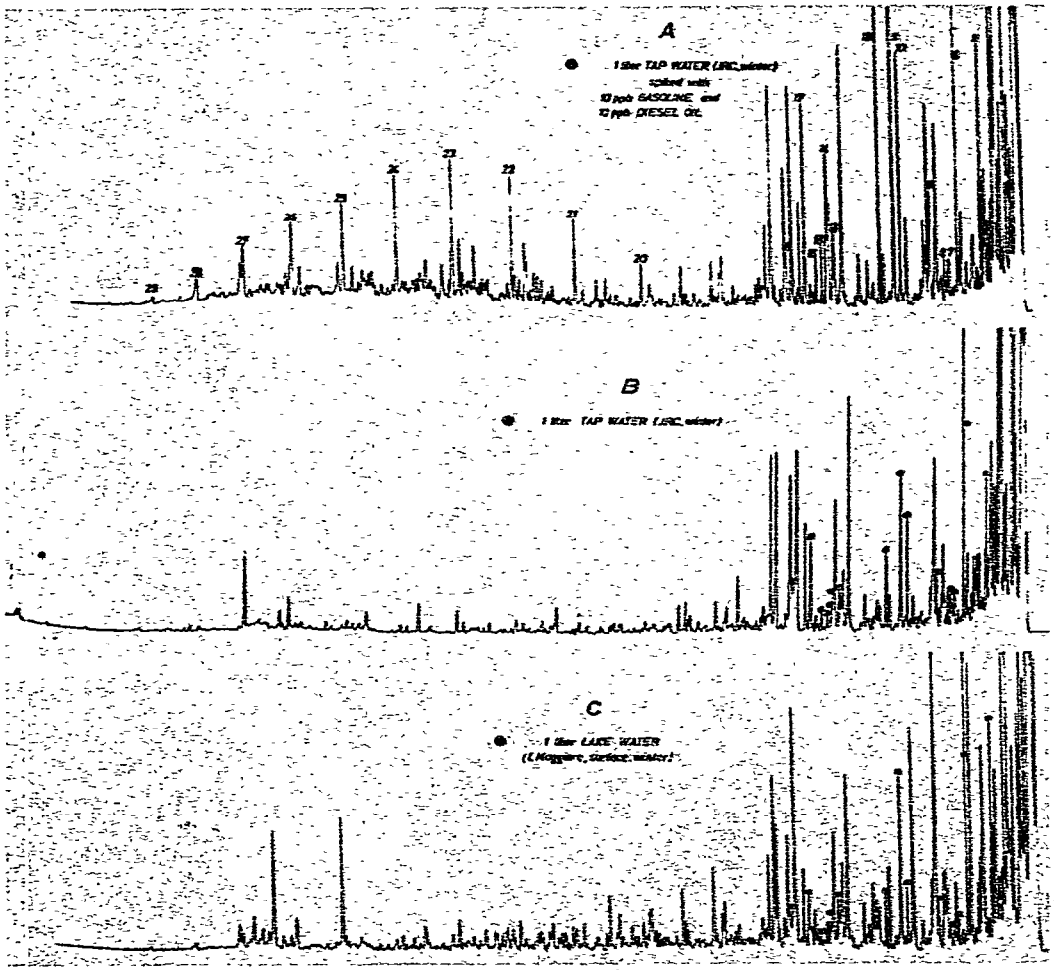

Fig. 9.

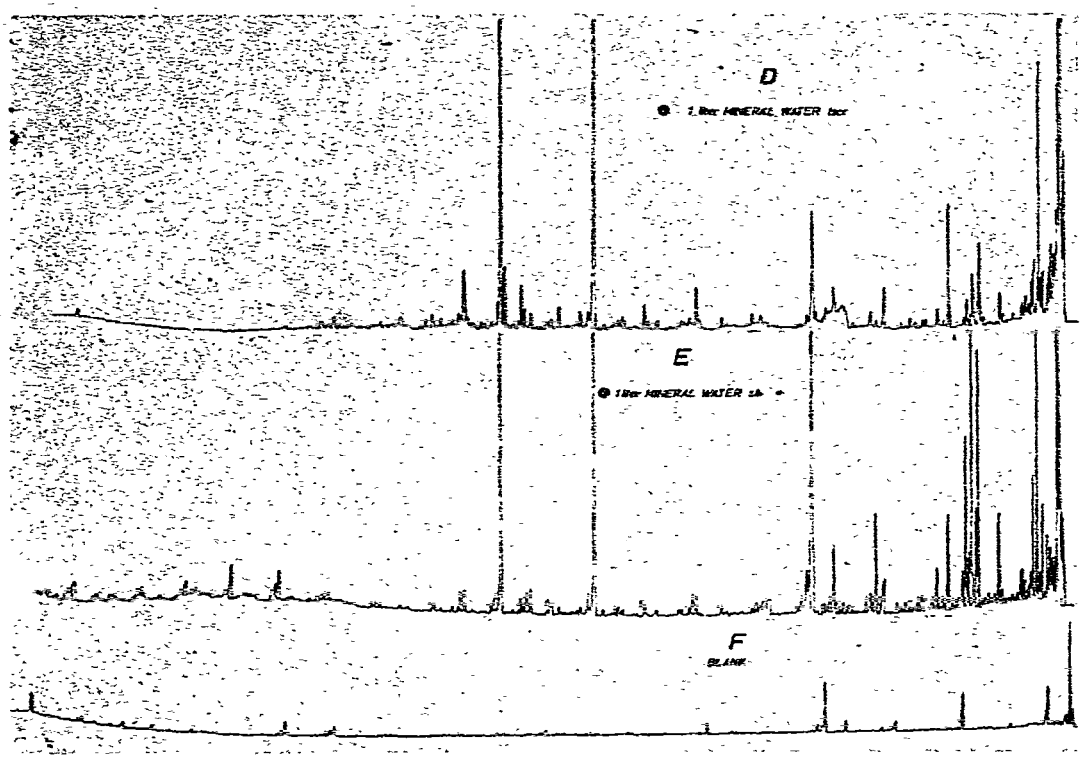

Fig. 9. Profiles of organic compounds in water. (A), 1 l of tap water spiked with 10 ppb of gasoline and 10 ppb of diesel oil; numbered peaks are those in Table III; (B), 1 l of tap water; (C), 1 l of Lake Maggiore surface water (winter) (this watter is used to produce tap water B); (D), 1 l of bottled mineral water from company LSCR; (E), 1 l of bottled mineral water from company SB; (F), Tenax column blank. Chromatographic conditions as in Fig. 7.

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