Journal of Chromatography A, 657 (1993) 155–164
Elsevier Science Publishers B.V., Amsterdam

CHROM. 25 214

Evaluation and optimization of the automatic thermal desorption method in the gas chromatographic determination of plant volatile compounds☆

Joaquín L. Esteban, Isabel Martínez-Castro and Jesús Sanz*

Instituto de Química Orgánica General (CSIC), Juan de la Cierva 3, 28006 Madrid (Spain)

(First received December 10th, 1992; revised manuscript received April 14th, 1993)

ABSTRACT

The automatic thermal desorption (ATD) method was used in the gas chromatographic determination of the volatile components of plants. The reproducibility of the method was evaluated for several operating conditions; the results were better than those obtained with other sample preparation methods (simultaneous distillation–extraction and solvent extraction). Some applications of the ATD method in the gas chromatographic determination of volatile components of Umbelliferae seeds are also presented, including the determination of the enantiomeric forms of limonene.

INTRODUCTION

Gas chromatography (GC) is the method of choice for the analysis of the complex mixtures of volatile compounds usually present in plants; however, it requires as a preliminary step the elimination of the non-volatile material. Many methods have been used in the isolation of volatile compounds, the most important being headspace trapping, solvent extraction, steam distillation and supercritical fluid extraction.

Thermal desorption from the sample has also been widely used, as both the sample size and the time required for its preparation are greatly reduced. Many laboratory-made systems [1–3] have been developed; some suppliers of gas chromatographs include the thermal desorption system as a sophisticated method of sample introduction [4]. However, few studies evaluating the quantitative results of the methods based on thermal desorption of volatile compounds in plants have been carried out.

An absolute evaluation of any sample preparation system would require an accurate previous knowledge of the sample composition. This is very difficult for real samples, however, as any analytical method including a fractionation step can introduce a discriminating factor in the results. We present in this paper an evaluation of the quantitative performance of an automatic thermal desorption (ATD) system, focusing on a study of the reproducibility of the method under different operating conditions. The results are compared with those obtained by using other sample preparation techniques (solvent extraction and steam distillation), and the possibility of artifact formation caused by thermal decomposition in different samples is discussed.

EXPERIMENTAL

Plant samples

Chamaecyparis lawsoniana Parl. (Lawson cypress) was selected for the evaluation of the method, as a previous study using steam distilla-

* Corresponding author.

☆ Presented at the *21st Scientific Meeting of the Spanish Group of Chromatography and Related Techniques*, Granada, October 21–23, 1992.

0021-9673/93/$06.00

tion had shown that its leaves (readily available) contain a very complex mixture of mono-, sesqui- and diterpenes with molecular mass in the range 136–280. This range of volatile components could be considered to cover those of many aromatic plants, whose more usual components are mono- and sesquiterpenes. After drying, the leaves were ground and homogenized using a mechanical blender. Ground samples were kept refrigerated in closed vials until analysis.

Seeds of several Umbelliferae plants were also collected (*Thapsia villosa*, *Heracleum sphondylium*) or purchased (*Petroselinum crispum*).

Steam distillation

Samples (2–4 g) were distilled using the micro simultaneous distillation–extraction (SDE) method (Chrompack, Middelburg, Netherlands) described by Godefroot *et al.* [5]. Pentane was used as a non-polar solvent.

Extraction

Plant samples (10 g) were shaken with 100 ml of diethyl ether. The process was repeated and the extracts were washed, concentrated by evaporation to a volume of 100 ml, dried over sodium sulphate and filtered.

Gas chromatography

The gas chromatographic equipment included an AutoSystem Gas chromatograph, a Model 400 automatic thermal desorption system (ATD-400) (described in detail later) and a Nelson Model 1020 data processor, all supplied by Perkin-Elmer (Norwalk, CT, USA). Nitrogen was used as the carrier gas and flame ionization detection was used. A laboratory-made fused-silica capillary column (column A; 25 m × 0.22 mm I.D.) coated with methylsilicone OV-1 was programmed from 70 to 220°C at 4°C/min. For chiral separations, a laboratory-made fused-silica capillary column (column B; 20 m × 0.22 mm I.D.) coated with 10% permethylated β-cyclodextrin in OV-1701 as stationary phase was kept at 72°C for 15 min and then programmed to 220°C at 4°C/min.

Automatic thermal desorption

The ATD-400 is an automatic thermal desorption system developed by Perkin-Elmer for the introduction of samples into a GC system. Although basically designed for the determination of volatile contaminants in the atmosphere, it can also be applied to other analytical problems. A summary of its operating mode and of the instrumental settings used in this study are as follows.

The sample to be analysed has to be contained in a small capped tube (desorption cartridge). In our case, the plant sample (1–40 mg) is placed in the desorption cartridge, between two glass-wool plugs. After a leak test, the cartridge is heated (50–400°C) in a flow of inert gas (nitrogen) for a selected time (desorption time, 1–30 min). The volatiles are adsorbed on Tenax GC in a cold trap (−30°C), which can then be heated to 400°C in a few seconds, allowing rapid transfer to the GC capillary column through a heated (50–225°C) fused-silica line.

The flow rates through the system and the amount of volatiles transferred to the column can be controlled by means of two flow splitters; the first (inlet split) is placed between the sample cartridge and the cold trap and the second (outlet split) after the cold trap.

Gas chromatography–mass spectrometry (GC–MS)

GC–MS was carried out using an HP-5890 gas chromatograph coupled to an HP-5971A mass detector (Hewlett-Packard, Palo Alto, CA, USA). A fused-silica capillary column (column C; 12 m × 0.22 mm I.D.) with OV-1 as stationary phase, supplied by Hewlett-Packard, was kept at 70°C for 5 min and then programmed from 70 to 220°C at 6°C/min. Helium was used as the carrier gas.

Methodology

Sample components were characterized from their retention times; when possible, they were identified by comparing their mass spectra and chromatographic retentions with published data [6–9] and, in some instances, with analytical data from standard compounds. Determinations (percentage relative composition) were made directly from integrator peak areas.

Several analyses were also carried out in order to check the importance of incomplete transfer

of volatile components through the ATD system, thermal decomposition or artifact formation. Each series included a run with the sample cartridge, one or several runs with empty cartridges (blanks) and a final run at a high oven temperature with the first cartridge.

The reproducibility of the method was evaluated from the relative standard deviation (R.S.D.) determined for each component from quantitative data from a series of analyses.

Calculations were carried out on a PC microcomputer.

RESULTS

Preliminary experiments

The SDE method [5] and liquid solvent extraction, which are the most widely used methods in the fractionation of plant volatile components, were selected for comparison with the ATD method. Special attention was given first to the qualitative and quantitative differences found among them.

A volatile fraction of *Chamaecyparis lawsonniana* obtained by the SDE method was analysed by GC–MS using column C under the chromatographic conditions previously described. The volatile components of this plant had been already studied [10–12]; limonene was reported to be the main component in all instances (15–65%). Our results were significantly different, as oplopanonyl acetate was present at a 37.5% concentration (calculated from the total ion current trace). Table I lists the components identified or characterized from their retentions and mass spectra and their retention times under the GC–MS conditions mentioned earlier.

Fig. 1 shows the GC results (column A) with the (a) SDE, (b) diethyl ether extraction and (c and d) ATD methods.

The ATD trace (c) includes some peaks (marked with black spots in Fig. 1c) which do not appear in the other chromatograms. Most of these peaks were identified as furyl derivatives, and seem to arise from the thermal decomposition of the carbohydrates present in the plants. This was confirmed by some ATD–GC runs (using the same conditions) on plant samples containing no volatile compounds, as they presented the same peaks. When the oven temperature was decreased from 300°C (Fig. 1c) to 180°C (Fig. 1d), these peaks disappeared.

The size of peaks 28 and 29 in trace (c) decreased when the oven temperature was decreased to 180°C. These peaks were clearly present in the chromatograms of the SDE extracts (see Fig. 1a), but these were very small in

TABLE I

VOLATILE COMPOUNDS OF AN SDE EXTRACT OF *CHAMECYPARIS LAWSONNIANA* IDENTIFIED OR CHARACTERIZED FROM THEIR RETENTION TIMES AND MASS SPECTRA

Compounds marked with asterisks were used in the reproducibility studies. See text for GC–MS column and conditions.

No.	Compound	Retention time (min)
1*	α-Pinene	3.01
2	α-Fenchene	3.24
3*	Sabinene	3.73
4	β-Myrcene	4.17
5*	δ-3-Carene	4.76
6	*p*-Cymene	5.00
7*	(*R*)-(+)Limonene	5.31
8	γ-Terpinene	6.28
9	Terpinen-4-ol	10.28
10	*p*-Cymen-8-ol	13.22
11	Bornyl acetate	14.20
12*	Mol. mass 180	14.39
13	γ-Terpenyl acetate	16.10
14*	α-Terpenyl acetate	16.48
15*	Mol. mass 180	17.12
16*	*trans*-Caryophyllene	19.01
17	Mol. mass 204	19.22
18*	Thujopsene	19.36
19	α-Humulene	20.09
20*	Bicyclosesquiphellandrene	20.38
21*	Mol. mass 204	20.91
22	Mol. mass 204	21.39
23*	γ-Cadinene	21.54
24	Mol. mass 204	21.72
25*	Calamenene	22.06
26*	δ-Cadinene	22.29
27	Mol. mass 222	22.39
28*	β-Oplopenone	24.40
29*	β-Oplopenone isomer	25.17
30*	Oplopenonyl acetate	31.92
31*	Mol. mass 262	32.97
32*	Kaurene derivative	33.30
33*	Mol. mass 272	35.03

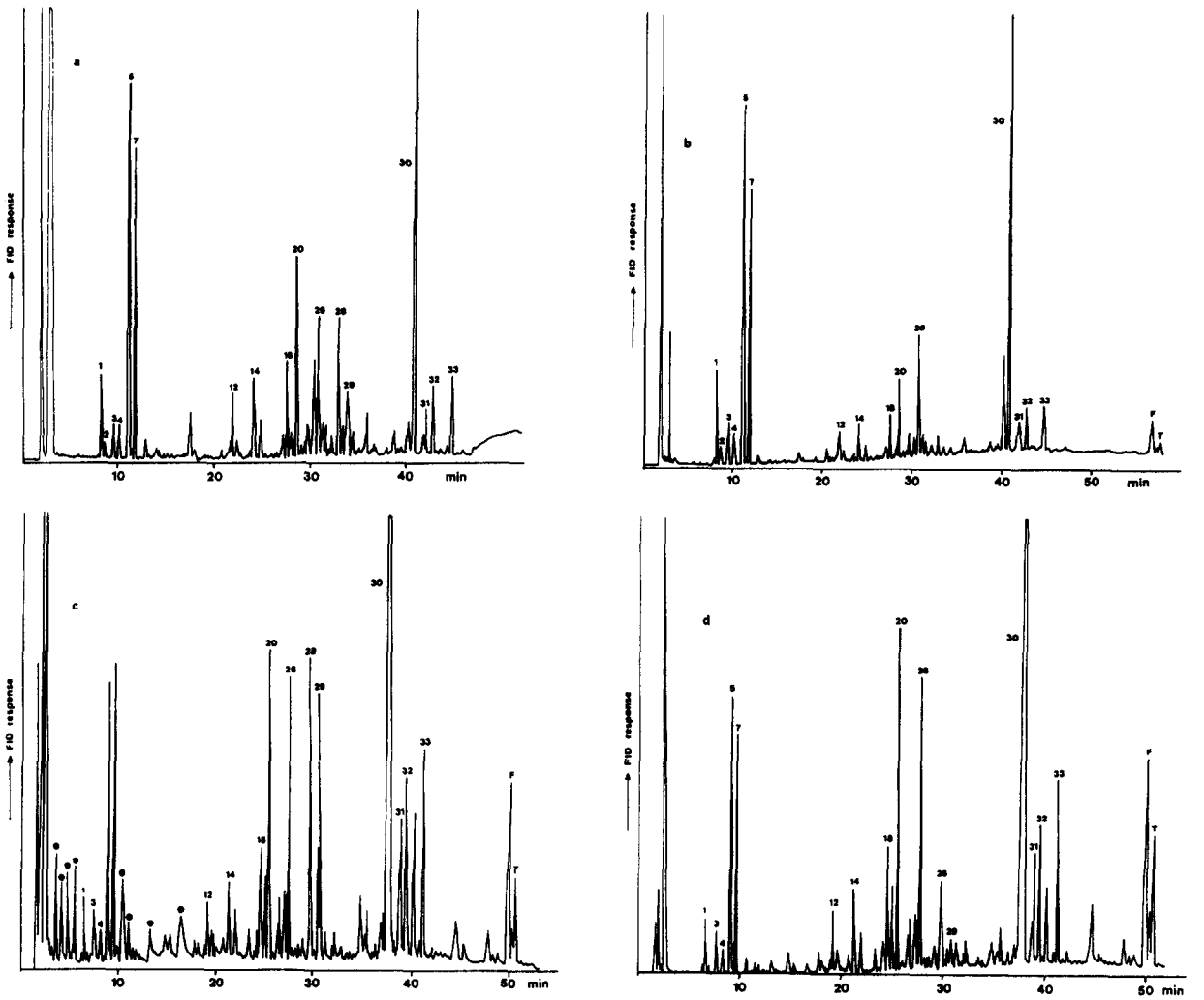

Fig. 1. GC traces of *Chamecyparis lawsonniana* volatile components obtained by different techniques: (a) SDE; (b) solvent extraction; (c) ATD (oven temperature 300°C); (d) ATD (oven temperature 180°C). See text for chromatographic conditions. Peak numbers as in Table I. F = ferruginol; T = totarol. Peaks marked with black spots correspond to thermal degradation compounds.

the solvent extract trace (b), thus seeming to be related to sample heating. Component 28 was identified as β-oplopenone by comparison of its mass spectrum with published data [13], while the mass spectrum of peak 29 seems to indicate a similar structure. In order to confirm that both components result from the thermal decomposition of the main component, oplopanonyl acetate, this compound was isolated by column chromatography as an almost pure compound and then submitted to an SDE extraction. When the resulting fraction was analysed by GC–MS, 4.5% of component 28 and 5.7% of component 29 appeared, showing that oplopanonyl acetate is partially decomposed by the SDE procedure; the ATD at low temperatures seems to decompose this compound to a lesser extent.

Peaks F (ferruginol) and T (totarol) appeared in both the diethyl ether extract and in the ATD traces, but not in that corresponding to the SDE fraction. Nevertheless, after an ATD run, they also appeared as small peaks in subsequent blank

TABLE II

EFFECT OF OPERATING PARAMETERS ON ATD RELATIVE CONCENTRATION (%) VALUES FOR DIFFERENT COMPOUNDS

(A) Oven temperature; (B) desorb flow-rate; (C) desorb time. Nr = Normal elution; Bl = blank; Cr = blank using the first cartridge. See text for details.

Compound No.	(A) Oven temperature (°C)											
	150			180			200			300		
	Nr	Bl	Cr	Nr	Bl	Cr	Nr	Bl	Cr	Nr	Bl	Cr
5	100	0	0	100	0	0	100	0	0	100	0	0
14	86.1	0	13.9	100	0	0	100	0	0	100	0	0
20	79.8	0	20.2	100	0	0	100	0	0	100	0	0
30	80.1	1.1	8.8	98.9	0.5	0.6	99.2	0.4	0.4	99.5	0.4	0.1
	(B) Desorb flow-rate (ml/min)											
	50			20			10			5		
	Nr	Bl	Cr	Nr	Bl	Cr	Nr	Bl	Cr	Nr	Bl	Cr
5	100	0	0	75.2	0	24.8	43.6	0	56.4	28.5	0	71.5
14	100	0	0	78.5	0	21.5	43.1	0	56.9	41.0	0	59.0
20	100	0	0	83	0	17.0	51.8	0	48.2	41.1	0	58.9
30	98.9	0.5	0.6	56.8	4.6	42.6	47.3	7.7	45.0	12.9	28.4	58.7
	(C) Desorb time (min)											
	15			11			8			4		
	Nr	Bl	Cr	Nr	Bl	Cr	Nr	Bl	Cr	Nr	Bl	Cr
5	100	0	0	96.3	0	3.7	91.5	0	8.5	92.9	0	7.1
14	100	0	0	99.9	0	0.1	99.9	0	0.1	95.0	0	5.0
20	100	0	0	97.8	0	2.2	96.0	0	4.0	94.4	0	5.6
30	98.9	0.5	0.6	97.7	1.0	1.3	95.3	2.3	2.4	76.3	9.6	4.1

Compound No.	(C) Desorb time (min)		
	2		
	Nr	Bl	Cr
5	91.4	0	8.6
14	94.6	0	5.4
20	92.9	0	7.1
30	26	43.2	30.8

runs, indicating contamination of the system. Several blank runs were required to eliminate their peaks.

Selection of desorption conditions

As high temperatures seem to produce sample and matrix artifacts, but low temperatures can give rise to incomplete elution of less volatile compounds, several ATD–GC series were run at different over temperatures, desorb flow-rates and desorb times in order to evaluate the effects of these parameters on the ATD elution. Each series included a run using the sample cartridge as usual, a blank run using an empty cartridge and a blank run using the original cartridge and a higher oven temperature (300°C). Several blank runs were included between series when necessary. The results are summarized in Table II; values for each component are expressed as its relative amount (%) in each run of the series.

TABLE III

MEAN RELATIVE VALUES (NORMALIZED TO $\Sigma = 100\%$) AND R.S.D. (EIGHT SERIES OF MEASUREMENTS, 20 SELECTED VOLATILE COMPONENTS)

See Table I for identification. Series A–E, ATD–GC. Common operating conditions: oven temperature, 180°C, desorb flow-rate, 50 ml/min; desorb time, 15 min. (A) Inlet split, 75 ml/min; outlet split, 50 ml/min; higher trap temperature, 320°C, sample size, 10 mg. (B) Inlet split, 75 ml/min; outlet split, 50 ml/min; higher trap temperature, 250°C; sample size, 10 mg. (C) Inlet split, 200 ml/min; outlet split, 100 ml/min; higher trap temperature, 320°C; sample size, 65 mg. (D) Inlet split, 100 ml/min; outlet split, 100 ml/min; higher trap temperature, 320°C; sample size, 40 mg. (E) Inlet split, 0 ml/min; outlet split, 50 ml/min; higher trap temperature, 320°C; sample size, 5 mg. Series F, SDE extract (same extract, four injections). Series G, SDE extracts (five extractions). Series H, solvent extracts (three extracts).

Component	Mean relative value							
	A	B	C	D	E	F	G	H
1	0.7	0.9	1.0	0.9	0.5	1.9	2.1	3.5
3	0.7	0.6	0.6	0.8	0.6	0.9	1.1	1.7
5	4.0	4.5	4.8	4.2	3.0	9.4	10.5	14.2
7	3.4	3.7	3.8	3.7	2.6	7.4	8.1	11.0
12	1.0	1.0	1.0	1.0	1.0	1.7	1.4	1.4
14	1.3	1.4	1.4	1.3	1.3	2.1	2.1	1.7
15	0.7	0.7	0.7	0.7	0.7	0.9	1.0	0.7
16	0.5	0.5	0.5	0.4	0.4	0.8	1.1	0.8
18	1.6	1.6	1.6	1.4	1.4	2.6	2.9	2.3
20	5.9	6.1	6.2	5.8	5.7	5.0	5.9	3.9
21	0.9	1.1	1.1	1.0	1.0	1.5	0.9	0.9
23	1.1	1.1	1.1	1.0	1.1	1.1	1.2	1.0
25	0.8	0.9	1.0	0.8	0.9	2.4	3.0	0.0
26	5.5	5.0	4.5	5.0	4.9	5.9	5.5	8.0
28	2.1	2.0	2.0	2.4	2.8	4.4	4.7	1.3
29	0.4	0.5	0.5	0.6	0.8	2.4	2.4	0.5
30	62.2	61.6	61.4	61.7	64.2	43.8	40.1	40.8
31	1.8	1.8	1.8	1.8	2.1	1.3	1.1	1.6
32	2.5	2.3	2.3	2.7	2.6	1.8	2.1	2.1
33	2.8	2.8	2.8	2.9	2.7	2.3	2.5	2.4
	R.S.D. (%)							
	A	B	C	D	E	F	G	H
1	9.4	21.2	7.8	14.9	20.9	5.7	19.6	12.7
3	2.0	17.6	13.0	13.7	10.0	9.0	17.9	12.2
5	7.4	13.7	5.2	12.4	10.1	4.4	15.6	10.6
7	7.7	10.8	4.6	16.0	12.8	5.3	14.3	10.2
12	5.0	6.8	1.5	6.0	8.5	21.7	10.6	17.9
14	2.3	6.1	2.1	6.2	6.5	3.0	7.3	3.1
15	8.1	8.7	8.9	12.2	8.7	9.6	6.8	4.7
16	2.0	7.6	1.5	13.4	6.5	22.7	20.9	24.5
18	3.3	3.9	2.7	7.5	10.1	5.0	6.4	1.5
20	1.0	1.9	3.2	3.0	5.8	0.5	7.9	3.6
21	5.2	3.3	5.5	5.2	8.5	17.0	15.0	20.1
23	3.0	4.6	6.6	4.8	5.7	10.1	4.8	26.2
25	6.6	7.2	9.7	11.3	16.0	1.3	12.4	0.0
26	2.5	5.9	4.3	8.8	9.2	2.3	13.0	4.6
28	6.8	17.6	17.7	10.2	8.2	5.5	4.1	2.7
29	19.4	11.7	10.8	24.7	17.0	21.9	26.0	13.0
30	0.9	2.0	1.2	1.8	2.3	3.2	11.8	5.6
31	2.7	2.9	3.9	4.5	21.1	18.2	15.5	26.6
32	3.8	3.4	3.4	5.5	4.8	2.4	7.8	8.1
33	2.7	3.2	1.8	7.9	5.0	4.4	7.3	3.9

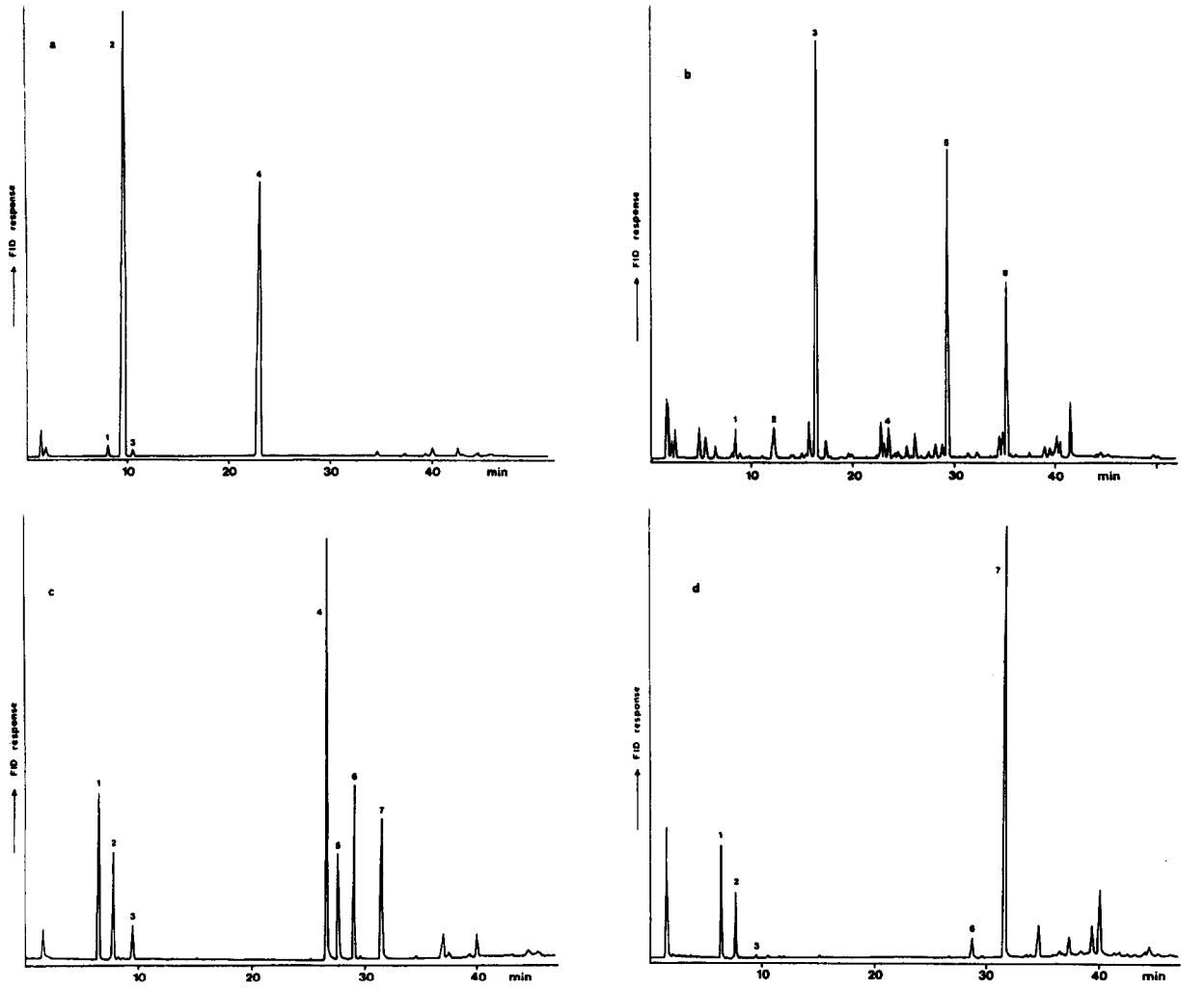

Fig. 2. ATD–GC traces of volatile components of Umbelliferae seeds. (a) *Thapsia villosa*: 1 = β-myrcene; 2 = limonene; 3 = α-terpinene; 4 = methylisoeugenol. (b) *Heracleum sphondylium*: 1 = isopropyl isobutyrate; 2 = isobutyl isopentanoate; 3 = *n*-octyl acetate; 4 = *n*-octyl butyrate; 5 = *n*-octyl hexanoate; 6 = *n*-octyl octanoate. (c) and (d) *Petroselinum crispum* (parsley): 1 = α-pinene; 2 = β-pinene; 3 = β-phellandrene; 4 = myristicine; 5 = trimethoxyallylbenzene; 6 = tetramethoxyallylbenzene; 7 = apiole. See text for chromatographic conditions.

The results of the first series (A, desorb flow-rate = 50 ml/min, desorb time = 15 min) indicate that components of medium and low volatility can be incompletely eluted at an oven temperature of 150°C. Taking into account the possibility of artifact formation at high oven temperatures, 180°C seem to be advisable for components of a broad volatility range. A lower oven temperature could be used with samples containing high-volatility compounds.

Series B in Table II (oven temperature = 180°C, desorb time = 15 min) show the importance of a high desorb flow-rate for complete elution from the sample cartridge of compounds of both high and low volatility. Flow-rates ≥50 ml/min seem to be advisable.

In series C (oven temperature = 180°C, desorb flow-rate = 50 ml/min), the negative effect of a short desorb time seems similar to, although less marked than, that of the desorb flow-rate. A

desorb time of 15 min seems to be advisable, as longer times at high temperatures could increase the danger of artifact formation.

Reproducibility

In order to evaluate the reproducibility of the ATD procedure, five series (A–E, each consisting of ten samples) of ATD–GC analyses were run. The values of the basic operating parameters were those recommended in the previous series: oven temperature 180°C, desorb flow-rate 15 ml/min and desorb time 15 min. The inlet split, outlet split and sample size were varied in order to determine the influence of possible sampling errors caused by plant sample heterogeneity on the reproducibility. Series F (SDE extract, four injections), series G (five SDE extracts) and series H (three solvent extracts) were also run for comparison purposes. For each series, mean values and R.S.D.s were calculated for the twenty selected compounds marked with asterisks in Table I; the results are given in Table III.

Although the quantitative elution pattern was similar for ATD, solvent extraction and SDE, the mean values for high-volatility compounds are in general higher for SDE and solvent extraction, whereas those of low-volatility compounds are higher for the ATD method. The best reproducibility was shown by series A and C (mean R.S.D.s 5.1% and 5.8%). The lower performance of the other ATD series was mainly caused by the high R.S.D.s for the most volatile components; since the mean R.S.D. was 9.9% for series E it seems that the use of too small amounts of plant material can introduce a sampling error. Hence the use of relatively high sample amounts with high splitting ratios seems to allow a satisfactory reproducibility.

Although the number of runs in the solvent extraction and SDE series is too small to draw statistical conclusions, it is clear that their reproducibility was lower (the R.S.D. was 8.7% for series F, 12.3% for series G and 10.6% for series H).

Example of application

The ATD–GC method was applied to the determination of the volatile components of seeds of the Umbelliferae family. The ATD operating conditions were those of series A in Table III. GC was carried out with column A using the previously described ATD and chromatographic conditions.

Seeds of *Thapsia villosa*, *Heracleum sphondylium* and parsley (*Petroselinum crispum*) were analysed. Approximately one quarter of a seed (1.5 mg) was introduced into the ATD cartridge for *T. villosa* and a single seed (6–7 mg) for *H. sphondylium*. Two different commercial samples of parlsey were analysed: 2–3 seeds (2–3 mg) were used.

The ATD composition (Fig. 2) was very similar in all instances to that found by SDE. No artifacts related to thermal decomposition were observed. The elution of volatile compounds was checked by running empty cartridges after each sample and was found to be complete.

The presence of different chemotypes and intermediate forms in parsley has been discussed recently [14]. Fig. 2c and d indicate that even using single seeds, chemical differences could be clearly shown by the ATD–GC method.

ATD also allowed the determination of chiral volatile compounds. One of the main volatile components of *Thapsia villosa* seeds is limonene (Fig. 2a). As this compound can be present in (*R*)-(+)- and (*S*)-(−)-forms, an ATD–GC analysis was carried out using column B, coated with a chiral phase. Fig. 3a shows the limonene peak obtained when about one quarter of a *Thapsia villosa* seed was analysed by ATD–GC. When the seed was spiked with (*R*)-(+)-limonene, a single limonene peak was also obtained. However, when the seed was spiked with (*S*)-(−)-limonene, a double peak appeared as shown in Fig. 3b. The retention times of both peaks corresponded to those found when injecting through the ATD a mixture of (*R*)-(+)- and (*S*)-(−)-limonene.

DISCUSSION

All sample fractionation procedures present advantages and drawbacks, which depend on the compounds to be analysed, their concentration in the sample and the possible effects of the matrix. In the case of plant volatile compounds, the main advantages of the ATD procedure are the possibility of carrying out a volatile frac-

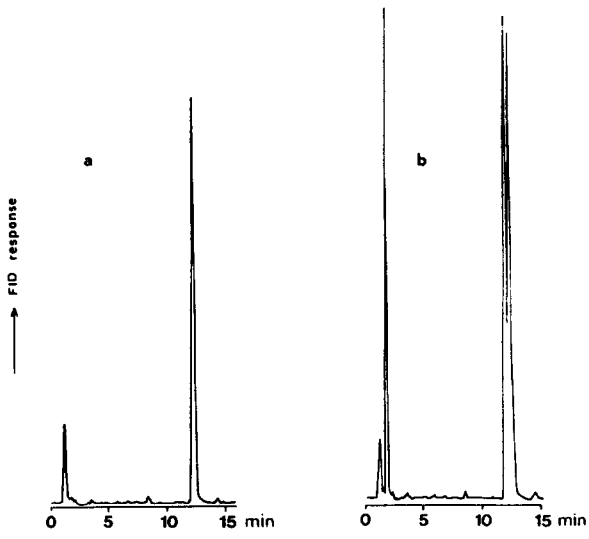

Fig. 3. ATD–GC determination of limonene in *Thapsia villosa* seeds using a chiral column. See text for chromatographic conditions. (a) *Thapsia villosa* seed; main peak is limonene. (b) *Thapsia villosa* seed spiked with (*S*)-(−)-limonene.

tionation on-line with the GC analysis, eliminating the need for a time-consuming extraction or fractionation step, and the small amount (1–20 mg, depending on volatile concentration) of plant required.

An additional advantage of the ATD method is its flexibility of use. Many operational parameters such as temperatures, flow-rates and splitting ratio can be changed, selecting their optimum values for a given application. Many possibilities of method implementation were not studied in this work, such as the introduction of plant solvent extracts into the ATD cartridge in order to avoid the artifacts produced from thermal decomposition of the insoluble compounds and the use of different adsorbents in the cold trap and of different packing materials for the plant in the sample cartridge.

When compared with other well established methods of plant volatile analysis, such as steam distillation and extraction, the ATD method, according to our results, presents better reproducibility probably because sample fractionation and introduction are carried out automatically.

Thermal decomposition of labile volatile compounds, which also occurs when using the SDE method, can be reduced in the ATD method while maintaining a high volatile recovery by selecting an oven temperature between 150 and 200°C. Thermal production of artifacts from the matrix is also very low at these temperatures.

Although liquid solvent extraction does not produce thermal decomposition, it is a slow technique that usually requires a concentration step; component recoveries can depend on the solvent used.

The method of choice when the sample contains thermally labile components seems to be supercritical fluid extraction, although in some instances extractable matrix components can interfere with GC analysis [15].

The possibility of system contamination is a drawback of the ATD method when compounds in the molecular mass range 300–400 are present in high concentrations in the sample. These compounds can be desorbed from the sample cartridge at 150–180°C, but they can partially remain in the system and appear in subsequent runs. The use of a lower oven temperature would result in incomplete desorption of compounds in the molecular mass range 200–300, which can have interesting flavour properties. A high desorb flow-rate would perhaps be necessary in the analysis of these samples.

We have applied the ATD method successfully to samples of different plant species. From our results, it seems to be useful when very large numbers of GC analyses are required in order to obtain results of statistical value and it is necessary to use only a small amount of plant. Possible applications include analytical studies on the distribution of volatile compounds in plants or chemotaxonomic studies based on their volatile composition. Once the instrument parameters have been optimized and the problems related to the specific application have been minimized, single plants (for chemotaxonomic studies) or parts of plants, flowers or leaves (for distribution studies) can be automatically analysed; when necessary, the use of chiral GC columns can allow the determination of enantiomeric composition.

ACKNOWLEDGEMENTS

This work was supported by the Comunidad Autónoma de Madrid (project No. C150/91)

and by the DGICYT (projects PB88-034 and PB91-0077-C03-02). We thank Dr. R. Morales (Jardín Botánico, CSIC, Madrid) for the botanical analysis of the plant samples used in this study and Dr. M.C. de la Torre (Instituto de Química Orgánica General, CSIC, Madrid) for the isolation and identification of oplopanonyl acetate. We also thank M.I. Jiménez for column preparation.

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