

Preconcentration of samples by steam distillation–solvent extraction at low temperature

Gracia P. Blanch, Marta Herraiz*, Guillermo Reglero and Javier Tabera

Instituto de Fermentaciones Industriales, C.S.I.C., Juan de la Cierva 3, Madrid 28006 (Spain)

ABSTRACT

Operation of a micro steam distillation–solvent extraction (SDE) device in two different modes, namely at reduced pressure and involving the concentration of the dynamic headspace resulting from purging the sample with an inert gas, was investigated. A notable advantage of the proposed micro SDE apparatus is that the use of extraction solvents denser or lighter than the sample solvent is feasible with only one configuration. The modified simplex method was used to improve the performance of the analytical procedure by optimization of several experimental conditions involved in the process.

INTRODUCTION

Sample preparation for the GC analysis of complex mixtures still remains a difficult step that can significantly alter the composition of the sample to be analysed. Obviously, the possibility of introducing qualitative or quantitative changes during sample preparation should be strongly avoided, as eventual losses of important compounds cannot be made up for in a later stage of the analytical procedure. Hence too severe treatments are in general unwise and even the use of extremely mild conditions may be required if thermolabile compounds are present in the sample or degradation products resulting from chemical reactions must be precluded.

The past few years have seen the development of different isolation and concentration techniques involving adsorption, absorption, distillation and extraction [1–4]. However, continuing interest in the investigation of preconcentration methods is engendered by the realization that there is not and probably never will be a single sample preparation procedure that is suitable for

all samples under all conditions. Therefore, careful selection of the preliminary isolation process which best suits the nature of the sample and the requirements of the analysis to be carried out is necessary.

Likens and Nickerson [5,6] described an apparatus for continuous steam distillation with constant liquid–liquid extraction of the distillate (SDE). Several modifications of the original design have subsequently been proposed [7–9] and also a micro version that permits operation with small amounts of extraction solvents without requiring enrichment by evaporation has been reported [10,11]. This micro SDE version has already been employed for the preconcentration of different types of samples [12–17].

Recently we proposed a further modification of the micro SDE device [18] which allows the use of solvents denser or lighter than the sample solvent with only one configuration, since both the distillation solvent and distillation sample arms enter the mixing chamber at the same height. The enlarged volume of this chamber, placed at the top of the apparatus, contributes to effective mixing of the sample and the extraction solvent vapour.

A further interesting feature of the device is

* Corresponding author.

the introduction of a water-jacket concentric with a cold finger, which significantly increases the condenser surface available in the former SDE micro version [10,11]. As a result, the cooling system allows losses of the most volatile compounds to be minimized. Operation at normal pressure was optimized and excellent recoveries were, in general, obtained for several compounds of different polarities, volatilities and water solubilities [18].

As far as optimization procedures for analytical techniques are concerned, the use of the sequential simplex method [19] has already proved its usefulness for adjusting the controlling variables affecting a particular process so that some results achieve the best possible level [18,20–24].

In this work, we investigated the scope of the new micro SDE for operation both at reduced pressure or involving the concentration of the dynamic headspace from the sample in the aeration mode of operation [3]. For this purpose, optimizations of the experimental conditions involved in both approaches were accomplished by using the modified simplex procedure [25].

EXPERIMENTAL

Steam distillation–solvent extraction

The SDE apparatus used in this study was constructed in our laboratory by modifying the design of Godefroot *et al.* [10]. A detailed description of the new version was presented in a previous paper [18].

The test mixture consisted of fourteen compounds covering a wide range of polarity and volatility (see Table III for composition). A stock solution containing about 7.14% of each pure component was stored at -30°C in the dark. Test solutions having concentrations of 1 mg/l of each compound were obtained by adding an appropriate volume of the stock solution to 100 ml of water purified in a Milli-Q system (Millipore).

All reagents were of GC grade and were purchased from Merck (Darmstadt, Germany) (isoamyl acetate, ethyl hexanoate, ethyl octanoate, benzaldehyde, diethyl succinate, ethyl

dodecanoate, 2-phenylethanol), Aldrich Chemie (Steinheim, Germany) (1-hexanol, linalool, α -terpinol, γ -decalactone) and Sigma (St. Louis, MO, USA) (β -ionone, ethyl tetradecanoate).

In all instances, *ca.* 100 ml of test solution (containing 1 mg/l of each compound) were heated on a water-bath and 2 ml of freshly doubly distilled dichloromethane (Merck) distilled at the same time. Cleaned boiling chips were added to the sample and solvent flasks. Vapours of sample and solvent were condensed by the cold finger and the concentric water-jacket, as mentioned above. When enrichment was complete, all the steam distillable material present in 100 ml of the test solution was collected in *ca.* 2 ml of dichloromethane. Consequently, concentration by a factor of 50 was finally achieved.

Methyl octanoate (Fluka, Buchs, Switzerland) (0.1 μl) and methyl decanoate (Fluka) (0.1 μl) were added as internal standards to the extracted compounds.

After finishing the extraction time, a further concentration step was not necessary [10,11,18] and the GC analysis was subsequently performed by sampling a 2- μl volume of the obtained extract.

The SDE was rinsed with acetone (Merck, Darmstadt, Germany) and Milli-Q-purified water between consecutive runs.

Preparation of banana extracts

Ripe peeled bananas (*Musa cavendishii* var. *enana*) from the local market (about 50 g), the same amount of $(\text{NH}_4)_2\text{SO}_4$ (enzymic inhibition) (26) and 100-ml of water purified in a Milli-Q system were homogenized. The sample was placed in a 500-ml flask and a 2-ml volume of twice-distilled dichloromethane was used as extracting solvent.

After finishing the enrichment step a 0.2- μl volume of methyl octanoate (internal standard) was added to the extracted compounds and subsequently 0.5- μl of the banana extract was chromatographed.

The SDE operation was performed in experimental conditions selected after the optimization procedure described below.

Capillary gas chromatography–mass spectrometry

All samples were analysed by gas chromatography using a 50 m × 0.22 mm I.D. fused-silica capillary column (SGE, Ringwood, Australia) coated with a 0.25- μ m layer of cross-linked BP-21 (FFAP). A Perkin-Elmer Model 8500 gas chromatograph provided with a Perkin-Elmer PTV injector and a flame ionization detector, operated at 250°C, were used. The equipment was coupled to a Model 2600 chromatography software system (Nelson Analytical). Helium at 40 p.s.i.g. (1 p.s.i. = 6894.76 Pa) served as the carrier gas.

The temperature of the chromatographic column was first kept at 70°C for 5 min, then raised at 5°C/min to 180°C. This final temperature was held for 15 min. In all instances, injections were carried out in the cold split (1:10) mode by maintaining the vaporizer at 30°C on injection. This temperature was increased at 14°C/s to 250°C.

To confirm peak identification, the gas chromatograph was linked to a Perkin-Elmer ITD-50 ion-trap detector (electron impact, 70 eV). The column and chromatographic conditions were the same as above.

Compounds were identified by comparison of spectra with those of the NBS (National Bureau of Standards) library. Moreover, most components were identified by matching the spectral data with those of authentic reference compounds analysed under identical conditions.

Simplex optimization

According to Spendley *et al.* [27], the initial experimental design (initial simplex) was established after fixing the initial values for each of the selected variables (termed factors). The experimental points defining the first simplex are thus located by establishing values for the factors such that the points lie at the vertices of a regular simplex of the required dimensionality.

Eqn. 1 was used to calculate physical values of the factors from their mathematical coordinates:

$$X_{\text{phys}} = X_0 + X_{\text{mat}}s \quad (1)$$

where X_{phys} is the physical value of variable X , X_{math} the corresponding mathematical coordi-

nate, X_0 its base level (starting physical value) and s is the step size.

The selection of the factors to be optimized was based on a prior knowledge of the system or on preliminary experimentation. The step size was chosen arbitrarily but it was intended that the step should produce for each factor a comparable change in response.

After running the first simplex, the worst experimental value was eliminated and a new vertex was defined to form a new simplex with the retained vertices. This new vertex was obtained by modifying the simplex in the direction opposite to the undesirable result. If we define C as the centroid of the retained vertices in the movement and V_i as the rejected vertex, then the coordinates of the new vertex (V_i^*) can be calculated from the equation

$$V_i^* = C + \alpha(C - V_i) \quad (2)$$

where α is a factor by which the volume of the simplex is changed by the operations of reflection ($\alpha = 1$), contraction ($\alpha < 1$) or expansion ($\alpha > 1$).

Subsequently, the simplex design is applied in the direction given by the rules of movement of the modified simplex until the region of the optimum is located. In all instances, a minimum of two replicates of each analysis were performed.

RESULTS AND DISCUSSION

Table I shows the variables, base levels and step sizes considered in the optimization study of the micro SDE device operated at reduced pressure.

In order to evaluate how each modification of the selected variables affects the final results, the response value (R) defined in eqn. 3 was calculated after each experimental run.

$$R = \frac{\sum(C_i - C_i^0)^2}{n} + 800T \quad (3)$$

where C_i is the concentration of the considered compound, C_i^0 is the expected concentration of the same compound, n is double the number of replicates performed for each experimental point and T is the sample heating bath temperature. It

TABLE I

VARIABLES, BASE LEVELS AND STEP SIZES CONSIDERED IN THE OPTIMIZATION STUDY OF THE SDE PROCEDURE AT REDUCED PRESSURE

Variable	Base level	Step size
Sample heating bath temperature, T ($^{\circ}\text{C}$)	75	10
Solvent heating bath temperature, T_s ($^{\circ}\text{C}$)	7	10
Coolant temperature, T_c ($^{\circ}\text{C}$)	-7	5
Extraction time, t (min)	90	15
Pressure, P (mmHg; 1 mm Hg = 133.322 Pa)	206	50

should be noted that differences between the concentration of a compound and its corresponding expected value were squared to magnify errors affecting quantification. On the other hand, it was intended that the simplex should progress towards low sample heating bath temperatures since our objective was to develop a procedure suitable for the preconcentration of thermolabile compounds. For this purpose, the temperature was weighted with a factor of 800, which was established from previous experimentation. Obviously, the simplex optimization refers here to the minimization of the response function. In all cases, two different internal standards (methyl octanoate and methyl decanoate) were used to quantify each compound in each replicate.

Data obtained through the simplex optimization procedure are given in Table II. Previous considerations concerning the constraints for the system (*i.e.*, the boundaries on the variables which cannot or should not be crossed) suggested that we should not accept values higher than 90°C for the sample heating bath temperature in order to avoid artefact formation. Coolant temperatures lower than -10°C were also considered to be outside the experimental region owing to the temperature limitation of the equipment. According to the rules of the modified simplex method, any step that represents a boundary violation should be rejected without

experimentation and the response at this point is considered to be the worst in the corresponding simplex.

With regard to the data in Table II, several observations can be made. After performing the initial simplex (defined by the first six experiments in Table II), vertex 4 was rejected as it provided the worst (highest) value of the response function. The new simplex was then formed by using the retained vertices besides that resulting from reflecting the rejected vertex. As can be seen in Table II, at vertex 7 the response is the best in the simplex, so it is expanded using $\alpha = 2$, thus resulting in vertex 8 [24,25]. Further expansions with different values of α give rise to vertices 18 and 19. In contrast, vertices 11, 14, 16, 21 and 24 resulted from different contractions. At vertices 10, 15, 20 and 23, the response was the worst in the new simplex and also worse than the worst response in the previous simplex, so the simplex was contracted and its direction was reversed ($\alpha = -0.5$). However, at vertex 13, the response was the worst in the new simplex but not worse than the worst response in the previous simplex, so the simplex was contracted but its direction was not reversed ($\alpha = 0.5$). It should be noted that experiment 10 was treated as a constraint owing to the inadequate rate of solvent evaporation, and therefore it was considered to produce the worst response in the simplex.

The simplex optimization procedure was stopped after vertex 24 because from vertex 18 onwards insignificant improvements in the response value were obtained, suggesting that the optimum had been attained. Finally, the experimental conditions defining experiment 18 (*i.e.*, sample heating bath temperature 84.2°C , solvent heating bath temperature 18.8°C , coolant temperature -7.7°C , extraction time 93 min, pressure 149 mmHg) should be considered as the most suitable, as they provide the lowest response value. Under these conditions, the sample temperature is actually 60°C .

Table III gives the recoveries and the relative standard deviations (R.S.D.s) obtained for the extracted compounds under the optimized conditions for the SDE operated at reduced pressure. It is worth emphasizing that the high solubility in

TABLE II
SIMPLEX STEPS FOR THE OPTIMIZATION OF THE SDE PROCEDURE AT REDUCED PRESSURE

Vertex No.	Simplex No.	Retained vertices	Experimental variable levels					Response
			T (°C)	T_s (°C)	T_c (°C)	t (min)	P (mmHg)	
1	1	—	75.0	7.0	−7.0	90	206	89 739
2	1	—	84.1	9.0	−6.0	93	196	79 941, 78 852 ^e
3	1	—	77.0	16.1	−6.0	93	196	81 138
4	1	—	77.0	9.0	−2.4	93	196	90 929
5	1	—	77.0	9.0	−6.0	104	196	90 070
6	1	—	77.0	9.0	−6.0	93	160	75 651, 75 235 ^e
7	2	1,2,3,5,6	79.1	11.1	−9.9	96	186	75 028, 74 074 ^e
8 ^a	2	1,2,3,5,6	80.1	12.1	−13.7	98	181	— ^f
9	3	1,2,3,6,7	79.9	11.9	−8.0	82	182	75 155, 77 417 ^e
10	4	2,3,6,7,9	83.9	15.9	−7.3	93	162	— ^g
11 ^b	4	2,3,6,7,9	77.2	9.2	−7.1	91	195	93 772
12	5	2,6,7,9,10	84.5	6.6	−8.9	90	158	75 399, 75 469 ^e
13	6	2,6,7,9,12	78.0	3.2	−8.2	89	191	95 535
14 ^c	6	2,6,7,9,12	79.5	6.4	−8.0	90	184	96 811
15	7	6,7,9,12,13	75.3	7.7	−10.4	87	155	— ^f
16 ^b	7	6,7,9,12,13	81.9	8.7	−7.1	92	186	76 980
17	8	6,7,9,12,16	83.0	15.7	−7.8	92	158	72 879
18 ^d	8	6,7,9,12,16	84.2	18.8	−7.7	93	149	72 214, 72 464 ^e
19 ^a	8	6,7,9,12,16	85.5	22.0	−7.6	94	141	72 949
20	9	6,7,12,16,18	82.8	9.9	−7.8	103	154	85 253
21 ^b	9	6,7,12,16,18	80.6	11.4	−7.9	88	175	78 939
22	10	6,7,12,18,20	81.2	13.5	−9.0	99	138	83 611
23	11	6,7,12,18,22	79.6	13.8	−8.8	85	162	85 935
24 ^b	11	6,7,12,18,22	82.0	10.8	−8.1	99	156	74 425

^a Obtained from expansion, $\alpha = 2.0$.

^b Obtained from contraction, $\alpha = -0.5$.

^c Obtained from contraction, $\alpha = 0.5$.

^d Obtained from expansion, $\alpha = 1.5$.

^e The second response value is the mean value obtained after performing a new run to check a vertex maintained $K + 1$ movements [26], where K is the number of variables.

^f Constraint. Rejected without experimentation owing to temperature limitation of the equipment (coolant temperature).

^g Considered as a constraint. Rejected owing to inadequate evaporation of the solvent.

water of 2-phenylethanol might be the cause of its low recovery.

As far as the optimization of the SDE operation in the aeration mode is concerned, the variables considered to be most relevant are given in Table IV. It should be noted that the sample temperature was held constant (40°C) throughout the simplex procedure, as the use intended for the optimized system demands the extraction of thermally unstable substances.

The response function (R') used in this optimi-

zation can be expressed as

$$R' = \frac{\sum (C_i - C_i^0)^2}{n} \quad (4)$$

where the symbols are defined as in eqn. 3.

Before starting the experimentation, it was decided to consider coolant temperatures lower than -10°C as a boundary violation, owing to the previously mentioned limitation of the equipment. Table V gives the set of experimental values tested in the optimization of the SDE

TABLE III

RECOVERIES AND RELATIVE STANDARD DEVIATIONS OBTAINED FOR THE COMPOUNDS SELECTED UNDER THE SIMPLEX-OPTIMIZED CONDITIONS CORRESPONDING TO THE SDE OPERATED AT REDUCED PRESSURE

Compound	Recovery (%) ^a	R.S.D. (%) ^b
Isoamyl acetate	94.59	8.87
Ethyl hexanoate	96.14	9.29
Terpinolene	51.98	22.19
1-Hexanol	95.45	10.59
Ethyl octanoate	98.50	14.08
Benzaldehyde	97.07	9.34
Linalool	99.55	10.84
Diethyl succinate	46.18	11.57
α -Terpineol	89.06	11.49
Ethyl dodecanoate	99.15	15.57
2-Phenylethanol	13.39	17.95
β -Ionone	98.83	14.96
Ethyl tetradecanoate	90.86	11.87
γ -Decalactone	48.96	13.43

^a Recovery as a percentage of initial amount. Mean value of ten replicates.

^b Calculated from ten replicates.

TABLE IV

VARIABLES, BASE LEVELS AND STEP SIZES CONSIDERED IN THE OPTIMIZATION STUDY OF THE SDE OPERATION IN THE AERATION MODE

Variable	Base level	Step size
Solvent heating bath temperature, T_s (°C)	50	10
Coolant temperature, T_c (°C)	-5	5
Extraction time, t (min)	90	20 ^a
Flow-rate of aeration gas, F (ml/min)	100	100

^a Modified to 60 after vertex 10 (see text for further details).

operation in the aeration mode and the values obtained for the response function. It must be noted that at vertex 11, the step size for the extraction time was changed from 20 to 60 because only during the actual experimentation did it become apparent that either the unit adopted for the mentioned factor was dispropor-

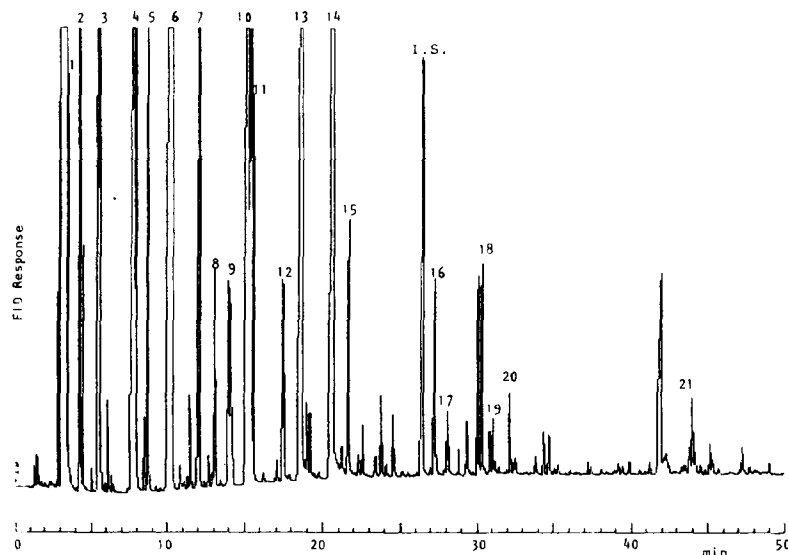


Fig. 1. Chromatogram of the aroma concentrate obtained from simultaneous steam distillation–solvent extraction (SDE) at reduced pressure of a banana by using dichloromethane. Experimental conditions for the SDE procedure corresponds to the simplex-optimized conditions in Table II (experiment No. 18). Column, 30 m \times 0.25 mm I.D. Carbowax 20M, film thickness 0.25 μ m (Quadrex); temperature 30°C (5 min), then increased at 3°C/min to 170°C; carrier gas, helium (25 p.s.i.g.); injection, split 1:50 (0.5 μ l). Peaks: 1 = ethyl acetate; 2 = 2-pentanone; 3 = isobutyl acetate; 4 = ethyl butanoate; 5 = butyl acetate; 6 = isoamyl acetate; 7 = isobutyl butyrate; 8 = heptan-2-one; 9 = butyl butyrate; 10 = isoamyl alcohol; 11 = 2-hexenal; 12 = 4-hepten-2-one; 13 = isopentyl butyrate; 14 = isopentyl 3-methylbutyrate; 15 = 4-hepten-2-ol acetate; 16 = hexyl butyrate; 17 = 3-methylbutyl hexanoate; 18 = 4-hepten-2-ol; 19 = 4-octen-2-ol acetate; 20 = 4-hepten-2-ol butyrate; 21 = 4-octen-1-ol. Internal standard (I.S.): methyl octanoate.

TABLE V
SIMPLEX STEPS FOR THE OPTIMIZATION OF THE SDE PROCEDURE IN THE AERATION MODE

Vertex No.	Simplex No.	Retained vertices	Experimental variable levels				Response
			T_s (°C)	T_c (°C)	t (min)	P (ml/min)	
1	1	–	50.0	–5.0	90	100.0	21 566
2	1	–	59.3	–3.9	94	121.8	19 374, 18 767 ^d
3	1	–	52.2	–0.4	94	121.8	18 989, 19 023 ^d
4	1	–	52.2	–3.9	108	121.8	23 633
5	1	–	52.2	–3.9	94	192.6	23 655
6	2	1,2,3,4	54.6	–2.7	99	40.2	20 309, 21 138 ^d
7	3	1,2,3,6	55.8	–2.1	80	70.1	21 012
8	4	2,3,6,7	61.0	0.5	94	77.0	25 896
9 ^a	4	2,3,6,7	52.7	–3.6	91	94.2	21 898
10	5	2,3,6,8	57.7	–1.2	111	110.4	26 625
11	6	2,3,6,11	55.8	–2.1	61	70.1	20 090
12	7	2,3,6,11	50.0	–5.0	90	100.0	18 656
13 ^b	7	2,3,6,11	44.5	–7.7	84	111.5	34 822
14 ^c	7	2,3,6,11	47.3	–6.4	87	105.8	16 895, 17 731 ^d
15	8	2,3,11,14	52.6	–3.7	59	169.6	19 034
16	9	2,3,14,15	49.8	–5.1	115	189.4	22 637
17 ^a	9	2,3,14,15	54.3	–2.8	75	99.9	21 073
18	10	2,3,14,16	51.6	–4.2	144	99.9	17 540, 16 695 ^d
19	11	2,3,14,18	55.3	–2.3	104	35.3	23 394
20 ^a	11	2,3,14,18	51.2	–4.4	112	150.9	20 150
21	12	2,3,14,18	54.0	–3.0	107	73.8	20 875
22 ^a	12	2,3,14,18	51.9	–4.1	111	131.6	22 404
23	13	2,14,18,21	53.9	–8.4	117	78.8	22 124
24	14	2,14,18,23	52.0	–8.4	119	129.3	21 316
25	15	2,14,18,24	51.6	–3.1	109	149.6	17 839

^a Obtained from contraction, $\alpha = -0.5$.

^b Obtained from expansion, $\alpha = 2.0$.

^c Obtained from expansion, $\alpha = 1.5$.

^d The second response value is the mean value obtained after performing a new run to check a vertex maintained $K + 1$ movements [26], where K is the number of variables.

tionately small or the system was relatively independent of its level. As can be seen in Table V, progress in the simplex is achieved through reflections, expansions and contractions performed as already described.

From Table V, it is also clear that the experimental conditions defining vertex 18 (*i.e.*, solvent heating bath temperature 51.6°C, coolant temperature –4.2°C, extraction time 144 min and flow-rate of aeration gas 99.9 ml/min) give the best response, so they were finally selected as the most suitable for the SDE operation which involves the concentration of the dynamic head-space resulting from purging the sample with an

inert gas. Under these optimized conditions, the recoveries and R.S.D.s given in Table VI were achieved. It is evident that the recoveries obtained for several compounds (diethyl succinate, α -terpineol, 2-phenylethanol and γ -decalactone) are extremely low and their corresponding R.S.D.s are unsatisfactory. However, the possibility of reliably determining some of the solutes in Table VI suggests that the optimized procedure is of interest for analysing samples avoiding the risk of undesirable chemical processes promoted by the sample temperature.

In order to illustrate the analytical capabilities of the optimized procedures, Figs. 1 and 2 depict

TABLE VI

RECOVERIES AND RELATIVE STANDARD DEVIATIONS OBTAINED FOR THE COMPOUNDS SELECTED UNDER THE SIMPLEX-OPTIMIZED CONDITIONS CORRESPONDING TO THE SDE PROCEDURE IN THE AERATION MODE

Compound	Recovery (%) ^a	R.S.D. (%) ^b
Isoamyl acetate	71.82	9.14
Ethyl hexanoate	72.63	7.65
Terpinolene	70.77	6.69
1-Hexanol	20.84	11.30
Ethyl octanoate	72.42	8.33
Benzaldehyde	24.96	10.13
Linalool	43.76	8.93
Diethyl succinate	1.92	30.90
α -Terpineol	9.24	18.23
Ethyl dodecanoate	66.50	7.62
2-Phenylethanol	1.78	50.24
β -Ionone	51.90	13.56
Ethyl tetradecanoate	20.31	15.96
γ -Decalactone	2.52	26.02

^a Recovery as a percentage of initial amount. Mean value of ten replicates.

^b Calculated from ten replicates.

the chromatograms obtained from simultaneous steam distillation–solvent extraction at reduced pressure and in the aeration mode, respectively, of a banana, using dichloromethane as the extraction solvent. It is interesting that the aroma of the extract obtained from the SDE operated in the aeration mode was very similar to that of the original sample, thus suggesting the usefulness of this procedure for extracting volatile compounds from different products. The overall procedure, including sample preparation, steam distillation–extraction under optimized conditions and capillary GC analysis, requires *ca.* 3 h.

CONCLUSIONS

The proposed SDE device has proved to be very versatile as it allows operation at normal pressure and at reduced pressure and the concentration of the dynamic headspace from the sample. Moreover, the design of the new version is such that losses of high-volatility compounds are minimized and only one configuration is

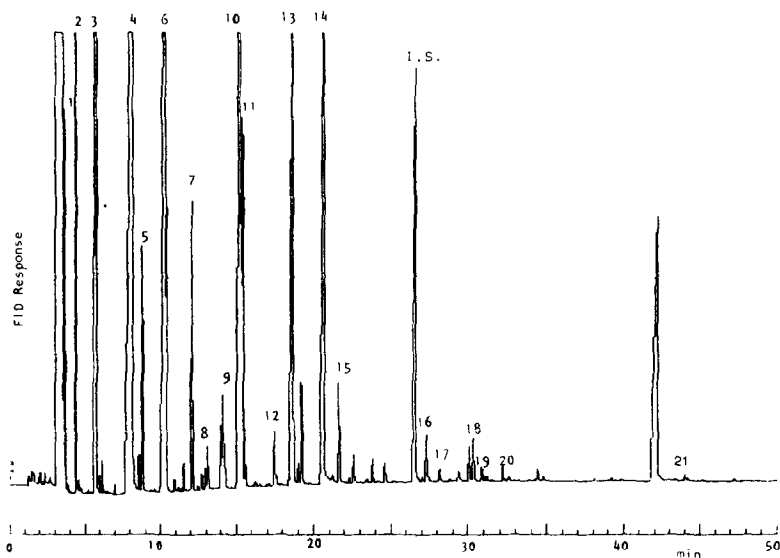


Fig. 2. Chromatogram of the aroma concentrate obtained from simultaneous steam distillation–solvent extraction (SDE) in the aeration mode of a banana by using dichloromethane. Experimental conditions for the SDE procedure correspond to the simplex-optimized conditions in Table V (experiment No. 18). The chromatographic analysis was performed under the same conditions as in Fig. 1. Peaks and internal standard as in Fig. 1.

required for using extraction solvents having densities either higher or lower than that of the sample solvent. A significant improvement in the performance of the SDE procedure was achieved by applying the sequential simplex method.

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