Food Chemistry, Vol. 56, No. 4, pp. 439–444, 1996
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0308-8146/96 $15.00+.00

0308-8146(95)00214-6

Analytical, Nutritional and Clinical Methods Section

# Rapid extraction of wine aroma compounds using a new simultaneous distillation–solvent extraction device

**Gracia P. Blanch, Guillermo Reglero & Marta Herraiz***

*Instituto de Fermentaciones Industriales, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

(Received 14 July 1995; revised version received and accepted 25 September 1995)

The potential of the simultaneous distillation–solvent extraction (SDE) technique for the rapid enrichment of wine aroma compounds was investigated. Several aspects concerning the extraction and concentration of volatiles from aqueous–alcoholic samples were studied and three different modes of operation, namely SDE at normal pressure, SDE at reduced pressure and SDE involving the concentration of the dynamic headspace resulting from purging the sample with an inert gas, are considered. A new SDE apparatus previously designed in our laboratory, to allow the use of extraction solvents denser or lighter than the solvent sample with only one configuration, was employed. Copyright © 1996 Elsevier Science Ltd

## INTRODUCTION

Recently, various concentration methods have been proposed for the analysis of volatile components of different sample matrices but it is generally admitted that none of them are suitable for all samples in all situations (Jennings & Rapp, 1983; Maarse & Belz, 1985; Poole & Schuette, 1983; Etievant *et al.*, 1986).

The chromatographic analysis of the volatile composition of wines poses a further analytical problem due to the fact that its second major compound (ethyl alcohol) produces a very large, tailing peak which may mask different compounds, thus making difficult or even hindering the achievement of a satisfactory chromatographic resolution. In this case, it is not only necessary to produce more concentrated samples but also to remove most of the ethyl alcohol without affecting the relative concentration of other volatile compounds. In addition to this, the wine aroma is a rather complicated fraction containing many components covering a wide range of volatilities, polarities and concentrations.

Liquid–liquid extraction (LLE) has been extensively used for obtaining exhaustive enrichment of volatile components including those occurring in alcoholic beverages (Hardy, 1969; Herraiz *et al.*, 1990*a,b,c*, 1991; Rapp *et al.*, 1976). However, it is a time-consuming and relatively laborious procedure which demands subsequent concentration of the solutes by evaporation of the solvent used during the extraction step. Losses of certain compounds by co-evaporation and eventual interferences in the chromatographic analysis, resulting from solvent impurities, have previously been described as eventual limitations of the liquid–liquid extraction procedure.

The simultaneous steam distillation–extraction technique (SDE) was first described in 1964 (Likens & Nickerson, 1964; Nickerson & Likens, 1966) and some modifications to the original apparatus have subsequently been suggested (Flath & Forrey, 1977; Maarse & Kepner, 1970; McLeod & Cave, 1975). The micro-SDE device proposed by Godefroot *et al.* (1981, 1982) allows operation with only a small volume of solvent without requiring further concentration of the extract prior to chromatographic analysis. The possibilities and limitations of the micro-SDE device as a pre-concentration technique for trace analysis of organics have been investigated and its usefulness for the enrichment of very different types of samples has previously been reported (Blanch *et al.*, 1991, 1992; Curvers *et al.*, 1984; de Frutos *et al.*, 1988; Green & Payne, 1989; Núñez & Bemelmans, 1984; Núñez *et al.*, 1984; Rijks *et al.*, 1983).

Recently we proposed a further modification of the micro-SDE device which offers a high volume mixing chamber, thus contributing to an effective mixing of the sample and solvent vapours (Blanch *et al.*, 1993*a,b*, 1994).

So far, however, the possibility of using the SDE technique for the pre-concentration of samples having a

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*To whom correspondence should be addressed.

relatively high alcohol content has hardly been investigated, probably due to the difficulty inherent in maintaining the demixing equilibrium which must be established between the two solvent layers (i.e. those corresponding to the solvent sample and the solvent used to collect all the steam distillable material) to make the experimentation possible.

The purpose of the present work was to study the feasibility of the new micro-SDE version, previously designed and constructed in our laboratory, for enrichment of wine aroma concentrates.

## MATERIALS AND METHODS

### Simultaneous distillation–extraction (SDE)

Wine aroma concentrates were obtained by using the micro-steam distillation–solvent extraction apparatus previously developed in our laboratory, which has been described elsewhere (Blanch *et al.*, 1993*b*). The SDE was operated in three different modes, namely at normal pressure, reduced pressure and involving the concentration of the dynamic headspace resulting from purging the sample with an inert gas (aeration mode).

To evaluate different extractive selectivities, two solvents (i.e. dichloromethane and *n*-pentane) were used. In all cases these solvents, purchased from Merck (Darmstadt, Germany), were doubly-distilled prior to use. In each experimental run, cleaned boiling chips were added to the sample and solvent flasks.

The SDE procedure was initiated by heating the wine sample by applying an oil bath. Simultaneously, a 2 ml volume of the extractive solvent distills by heating it with a water bath. The design of the SDE device allows both vapour and liquid-phase extraction to be performed while a continuous reflux of water and solvent is maintained during the extraction time. A subsequent concentration step was not demanded. The SDE apparatus was cleaned by rinsing it with acetone (Merck, Darmstadt, Germany) and Milli-Q-purified water (Millipore).

### Gas chromatographic analysis

A Perkin-Elmer Model 8500 gas chromatograph equipped with a PTV Perkin-Elmer injector and having the suitable software (Nelson Analytical) to integrate peak areas was used.

Throughout the experimentation, helium (18 psig) served as the carrier gas and the detector (FID) was maintained at 250°C. The PTV injector was kept at 30°C upon sample introduction and this temperature was subsequently increased (14°C/s) to 200°C (5 min). The injector was operated in the cold split mode (split ratio, 20:1) and in all cases the sampled volume was 5 $\mu$l.

A 30 m×0.25 mm ID fused silica capillary column coated with a 0.25-$\mu$m layer of Carbowax BTR (Quadrex, CT, USA) was used. The separation was performed by programming the column from 45°C (3 min isothermal) at 3°C/min to either 155°C (when using *n*-pentane as solvent) or 180°C (if dichloromethane is employed). The latter temperature (180°C) was maintained for 12 min while the analyses of the *n*-pentane extracts were finished just after reaching the final temperature (155°C).

## RESULTS AND DISCUSSION

The selection of experimental conditions affecting the operation of the new micro-SDE version was initially based on the results previously obtained in the optimization performed by using the modified sequential Simplex method (Blanch *et al.*, 1993*a,b*). Their study was carried out using a test mixture containing 14 compounds, typically found in wines, which were selected by considering differences in polarity, volatility and water solubility.

In the present study, however, a modification of some experimental variables was required due to the different vapour pressure of an aqueous–alcoholic mixture in comparison with that of the test mixture used in the previous optimization study. In each operation mode, different values were considered for the variables affecting the SDE experimentation and the following conditions were finally selected.

(a) *SDE—normal pressure*: sample heating bath temperature, 149°C; solvent heating bath temperature, 67°C; coolant temperature 3.4°C; and extraction time, 56 min.
(b) *SDE—reduced pressure*: sample heating bath temperature, 84°C; solvent heating bath temperature, 25°C; coolant temperature, −7.7°C; extraction time, 93 min; and pressure, 206 mmHg.
(c) *SDE—aeration mode*: solvent heating bath temperature, 52°C; coolant temperature, −4.2°C; extraction time, 144 min; and flow rate of aeration gas, 100 ml/min.

It should be underlined that in the new device, the distillation solvent and distillation sample arms enter the mixing chamber at the same height so that the use of extracting solvents having densities either higher or lower than that of the solvent sample is feasible with only one configuration. This aspect involves a clear advantage with respect to other micro-SDE versions that demand the use of different equipment depending on the density of the solvent to be used. Moreover, the new apparatus includes an enlarged surface water condenser which contributes to reduce eventual losses of high-volatile components.

The use of dichloromethane as the extracting solvent did not allow performance of the experimental run if a 100 ml volume of wine is placed in the sample flask. This is due to the fact that during the extraction, some ethyl alcohol from the sample flask gets into the demixing part, thus hindering the equilibrium between the two solvent layers (corresponding to water and dichloromethane) in the separation chamber of the SDE apparatus. The diminution of the alcohol content of the

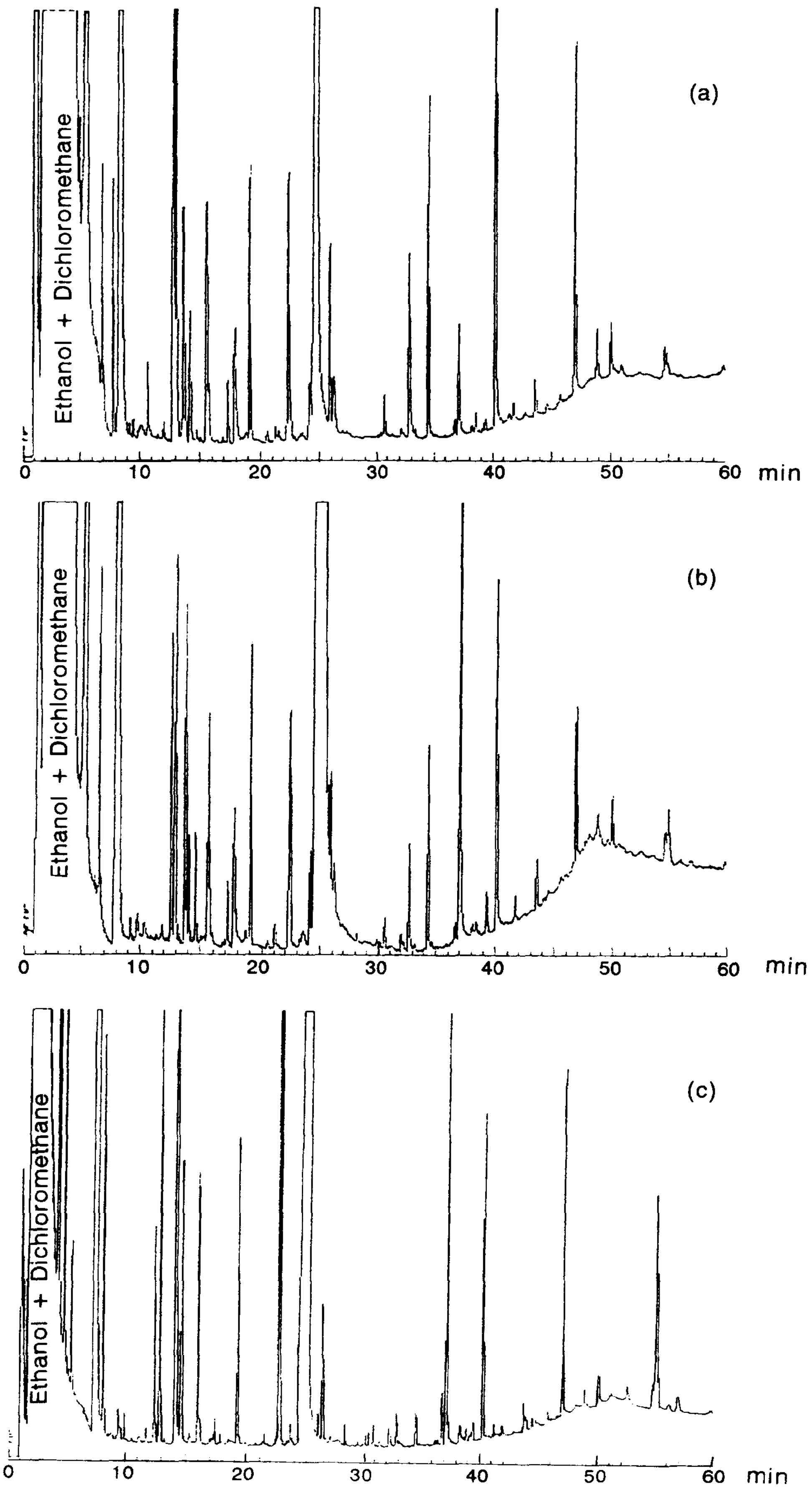

**Fig. 1.** Chromatograms of the aroma concentrates obtained from a 100 ml volume of a diluted white wine (1:1, v/v) by simultaneous steam distillation–solvent extraction (SDE) operated at (a) normal pressure, (b) reduced pressure and (c) in the aeration mode using dichloromethane (see text for further details).

sample simply by diluting the wine with water (1:1 v/v) grants the completion of the enrichment step. Further dilution of the sample (i.e. 1:3 v/v) makes the experimentation more convenient when unattended processing is required, although it is clear that lower enrichment factors will then be obtained.

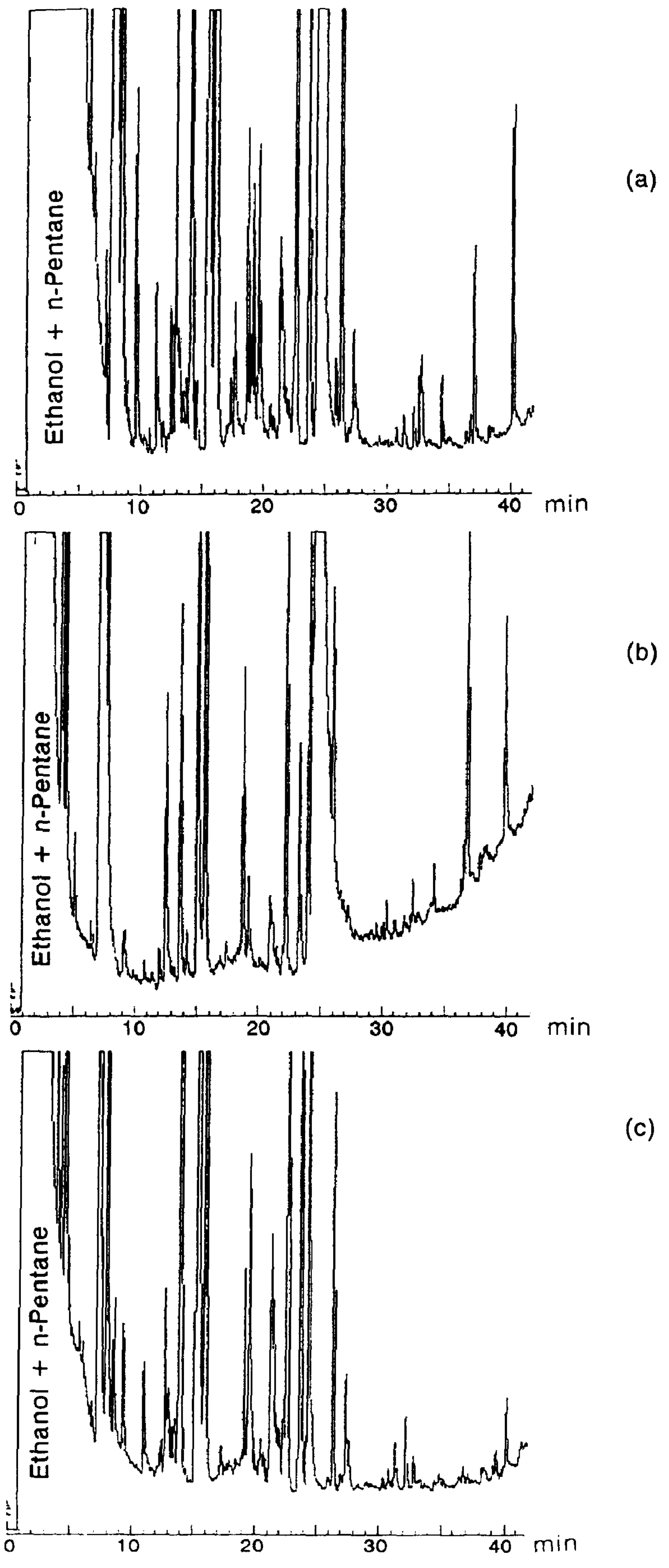

**Fig. 2.** Chromatograms of the SDE extracts obtained at (a) normal pressure, (b) reduced pressure and (c) in the aeration mode of a 300 ml volume of a white wine by using *n*-pentane (see text for further details).

Figure 1 gives the chromatograms of the aroma concentrates obtained from SDE, operated at the three different modes listed above, of a diluted (1:1, v/v) white wine (alcoholic content: 11% v/v), using dichloromethane.

As far as the experimentation with *n*-pentane as the extracting solvent is concerned, the lower solubility of ethyl alcohol in *n*-pentane compared with that for dichloromethane, allowed the maintenance of the required demixing equilibrium between water and *n*-pentane in the separation chamber of the SDE device. Consequently, the pre-concentration step could be succesfully completed even when a 100 ml volume of non-diluted wine was initially placed in the sample flask. Moreover, when using *n*-pentane, the SDE procedure can be satisfactorily performed from a higher volume (300 ml) of non-diluted wine (Fig. 2). In this respect, it is worthy to remark that the distance between sample and solvent flasks in the new SDE device (93 mm) facilitates not only their independent heating but also the possibility of performing the SDE operation, starting from quite high sample volumes, so that better enrichment factors can be finally achieved. Obviously, SDE operation using *n*-pentane can be also carried out from diluted wines, thus achieving lower concentration factors but, as a counterpart, less control of the separation chamber is demanded.

From Figs 1 and 2 it seems to be clear that, in principle, the three SDE operation modes investigated may be suitable for wine aroma analysis. According to our previous experience, operation at normal pressure may provide recoveries ranging from 79 to 100% for some compounds previously reported as wine aroma constituents (i.e. isoamyl acetate, ethyl hexanoate, terpinolene, 1-hexanol, ethyl octanoate, benzaldehyde, linalool, diethyl succinate, $\alpha$-terpineol, ethyl dodecanoate, $\beta$-ionone, ethyl tetradecanoate and $\gamma$-decalactone), relative standard deviations being lower than 10%. This operation mode, however, demands a higher sample temperature than that required if the experimentation is performed either at reduced pressure or in the aeration mode. This feature is evidently an important aspect to be considered if thermolabile solutes are analysed. Concerning the last two mentioned operation modes, we have also previously reported that SDE at reduced pressure allows higher recoveries (varying from 46 to 99% for the above-mentioned compounds) and lower relative standard deviations (average value: 12.6%) than SDE in the aeration mode (Blanch *et al.*, 1993*a*).

## CONCLUSIONS

The new micro-SDE apparatus used for this study allows extraction of wine aroma concentrates by operating in three different modes (i.e. at normal pressure, at reduced pressure and in the aeration mode). Experimentation with solvents having a density higher or lower than that of the solvent sample can be performed simply by changing the solvent and sample flask, which allows acquisition of complementary information by using solvents of different polarities, without requiring different configurations of the SDE device. One of the main advantages of the proposed method is that the overall procedure, including steam distillation–solvent extraction and capillary gas chromatographic analysis, is carried out in about 3 h and allows a significant enrichment of the wine simply by starting either from a small volume of a suitable extracting solvent or from a relatively high sample volume.

This preliminary study gives an insight into the possibilities of a simultaneous distillation and extraction technique for wine aroma analysis and, therefore, is far from comprehensive. Further research remains to be done mainly concerning the advantages of the proposed procedure over the current methodology. However, from these results it can be concluded that the method described here may offer several advantages for rapid wine aroma extraction, only demanding low volumes (i.e. 2 ml) of organic solvents.

## ACKNOWLEDGEMENTS

This work was made possible by financial assistance from the Comisión Interministerial de Ciencia y Tecnología (Project ALI 91/0621). G. P. Blanch is grateful to the Comunidad de Madrid for a grant.

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