Adsorption-Thermal Desorption-Gas Chromatography Applied to the Determination of Wine Aromas

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The application of adsorption-thermal desorption-gas chromatography to determine the heavy fraction of wine aromas is studied. The retention volume and the adsorption time suitable for our working conditions were established from standard solutions. A fast method that requires no sample manipulation is proposed for determining the volatiles of the heavy fraction of wine aromas.

INTRODUCTION

The low concentration of most of the volatile components of wine makes it necessary to extract and concentrate them before they can be analyzed by gas chromatography. Several extraction-concentration methods are used, among which are liquid-liquid extraction, simultaneous distillation-extraction, and headspace analysis. The advantages and disadvantages of these methods for analyzing volatile components have been the subject of several papers (Weurman, 1969; Hardy, 1969; Schreier et al., 1979; Núñez et al., 1984; Maarse et al., 1985; Frutos et al., 1988). Our experience has shown that in general these methods involve excessive sample manipulation, low reproducibility, and excessive time.

The use of adsorption on polymers as an extraction method for these volatile components has been widely studied (Leoni et al., 1976; Brown et al., 1979; Bertoni et al., 1981). This has led to other methods being used such as those that employ a programmable temperature vaporizer (PTV) provided with a quartz liner packed with different adsorbents over which the sample is adsorbed and desorbed (Vogt et al., 1979; Poy et al., 1981; Nitz et al., 1984; Herraiz et al., 1987; Villen et al., 1989; Blanch et al., 1991). Tenax (2,6-diphenyl-p-phenylene oxide) is an excellent adsorbent of wine volatiles because of its low water- and ethanol-adsorbing capacities (Janák et al., 1974) and its high adsorbing capacity for this type of compound (Brown et al., 1979). With some of these methods, not only does the drawback of having to introduce the sample into the column exist, but they also do not take into account the possibility of adsorbent saturation and the calibration with different concentrations of the same compound.

The purpose of this work is to apply the adsorption-thermal desorption-GC technique to measure wine aromas by bubbling an inert gas through a sample of wine. The aromas are automatically concentrated and immediately injected into a gas chromatograph, thus providing a rapid method for determining this type of compound with no manipulation.

MATERIALS AND METHODS

Samples. To optimize the experimental conditions, several compounds that generally appear in the chromatograms of wine using the same columns as used in this study were selected (Salinas et al., 1992). These were limonene, which is found at the beginning of the chromatogram, benzaldehyde and 2-phenethyl acetate from the center, and octanoic acid from the end. Figure 1 shows a chromatogram from a standard solution, in which the four chosen compounds are shown together with methyl octanoate, a substance used as internal standard (IS) and added in all of the
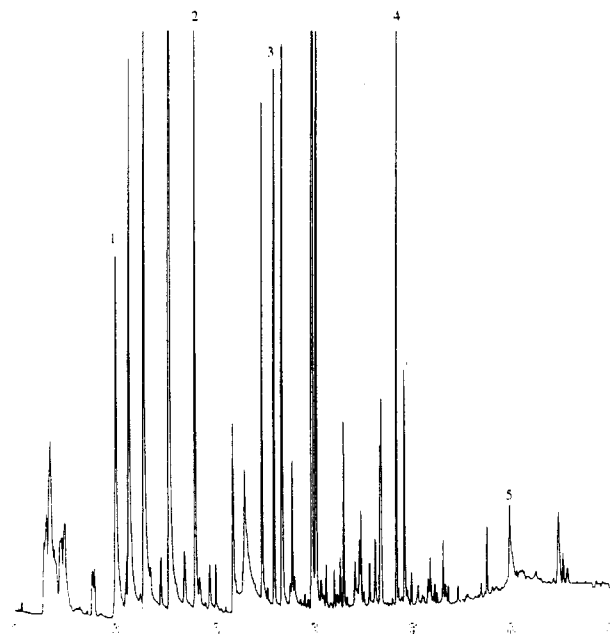

Figure 1. Chromatogram of standard solution: 1, limonene; 2, methyl octanoate (IS); 3, benzaldehyde; 4, 2-phenethyl acetate; 5, octanoic acid.
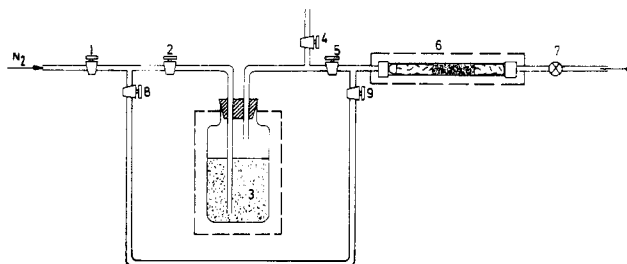

Figure 2. Adsorption scheme: 1, 2, 4, 5, 8, and 9, stop valve; 3, 50 cm³ of sample in a 30 °C bath; 6, metal tube containing 0.2 g of Tenax at 25 °C; 7, flow control. Line A: Volatile adsorption, 1 → 3 → 5 → 6 → 7. Line B: Ethanol and water elimination, 1 → 8 → 9 → 6 → 7.

analyses carried out immediately before adsorption in a proportion of 3 µL of a 5% solution in ethanol to 50 cm³ of sample.

For quantification, standard 12% solutions in ethanol were used containing the following compounds (Merck-GC): isoamyl acetate, limonene, *trans*-2-hexenal, ethyl hexanoate, ethyl pyruvate, hexyl acetate, ethyl heptanoate, hexanol, ethyl lactate, methyl octanoate (IS), *trans*-2-hexen-1-ol, heptanol, benzaldehyde, linalool, octanol, *cis*-3-hexen-1-ol, γ-butyrolactone, diethyl succinate, citronellol, α-terpineol, ethyl decanoate,

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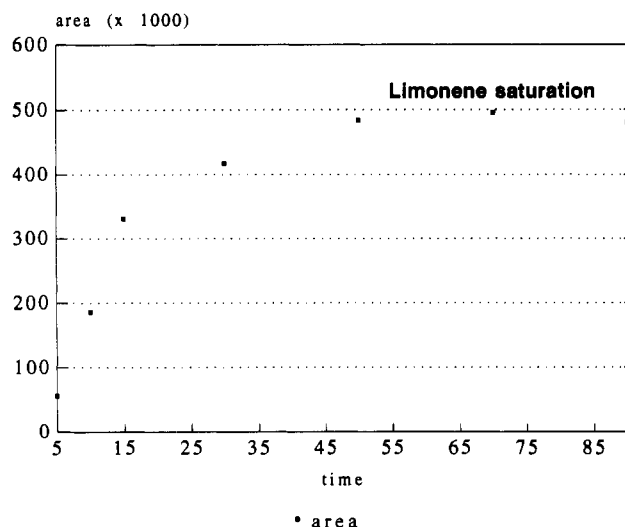
area (x 1000)

Limonene saturation

Figure 3. Evolution of peak areas for limonene with increasing adsorption times.

2-phenethyl acetate, ethyl laurate, hexanoic acid, benzyl alcohol, heptanoic acid, and octanoic acid.

Adsorption of Volatiles. The metal adsorption tube measured 88.9 mm × 6.35 mm o.d. × 4.50 mm i.d. and contained 0.2 g ± 0.01 g of Tenax-GC (60 mesh). The adsorbent was conditioned by passing N_2 through the tube at 340 °C with a flow rate of 30 mL/min for 6 h.

For adsorption of the volatile, the tube was connected to the instrumental device outlined in Figure 2. The vapor was drawn through the tube by bubbling dry N_2 over 50 cm^3 of sample at 30 °C. The approximate temperature of the tube was 25 °C. After the adsorption period, dry N_2 was passed through the tube to eliminate any remains of ethanol and water. The flow rate of
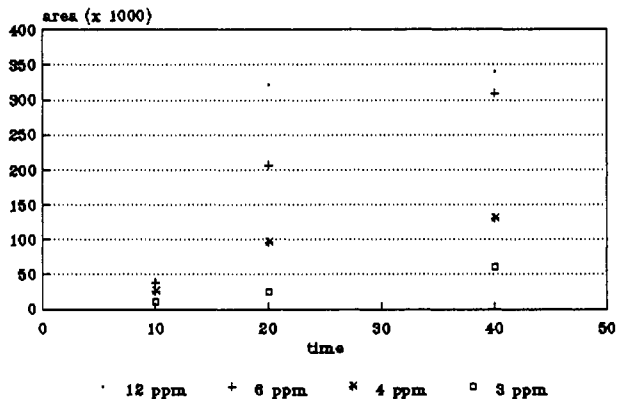
the N_2 was always 67 mL/min, which is within the range recommended for the tube dimensions used and for Tenax (Brown et al., 1979).

Instrumental. The packed tube was introduced into a (Perkim-Elmer) Spantech TD-4 thermal desorber coupled to a Perkim-Elmer 8310 gas chromatograph with a PTV injector and flame ionization detector. The following parameters were programmed: *(thermal desorption)* oven temperature, 300 °C; desorption time, 5 min; cold trap low temperature, –30 °C; cold trap high temperature, 350 °C; injection time, 40 s; transfer line temperature, 200 °C; trap adsorbent, Tenax (0.02 g).

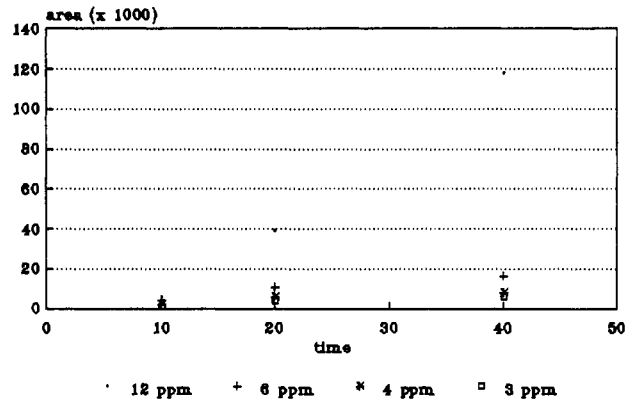*Gas Chromatography.* The chromatograph was equipped with a SGE 50 m × 0.22 mm i.d. fused silica capillary column coated with a 0.25-µm layer of cross-linked BP-21. The conditions were as follows: gas carrier, helium at 30 psig; temperature program, 50 °C, 2.5 °C/min, 180 °C, 8 min; injector program, –0.02 relay 1 ON, –0.01 PTV 200 °C; split ratio, 1:70: detector, 230 °C.
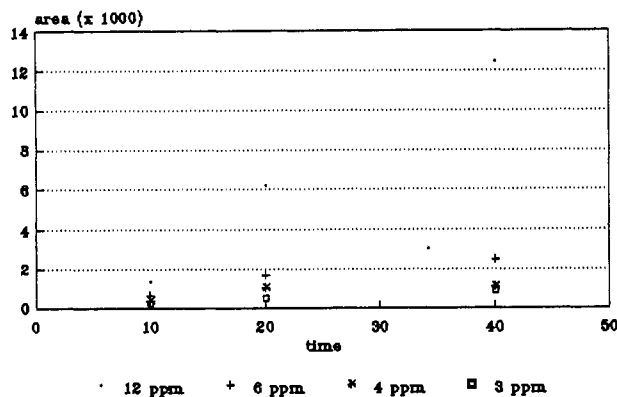
RESULTS AND DISCUSSION

The volume of gas needed to adsorb the compounds under study on the Tenax without risk of saturation was calculated first. This volume, called the safe sampling volume (V_s), is 50% of the retention volume (V_r), defined here as the point at which a single injection of vapor emerges from the tube. Since V_r depends on the boiling point of a compound (Brown et al., 1979), limonene (with the lowest boiling point) would have the lowest V_r in the standard sample used and the V_s of this substance would therefore be the limiting parameter in this study. The V_r of limonene is that for which the peak area obtained by chromatography remains constant when the volume of gas used for drawing the aromas in the adsorption process is increased. Figure 3 shows the area of the peaks obtained with solutions with a minimum of 3 ppm against the bubbling time of the nitrogen or desorption time (flow
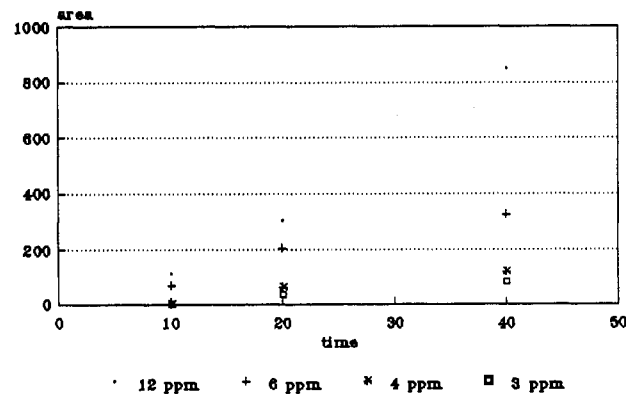
area (x 1000)

· 12 ppm + 6 ppm * 4 ppm □ 3 ppm

(a)

area (x 1000)

· 12 ppm + 6 ppm * 4 ppm □ 3 ppm

(b)

area (x 1000)

· 12 ppm + 6 ppm * 4 ppm □ 3 ppm

(c)

area

· 12 ppm + 6 ppm * 4 ppm □ 3 ppm

(d)

Figure 4. Evolution of peak areas for limonene (a), benzaldehyde (b), 2-phenethyl acetate (c), and octanoic acid (d) with increasing adsorption times and different concentrations.
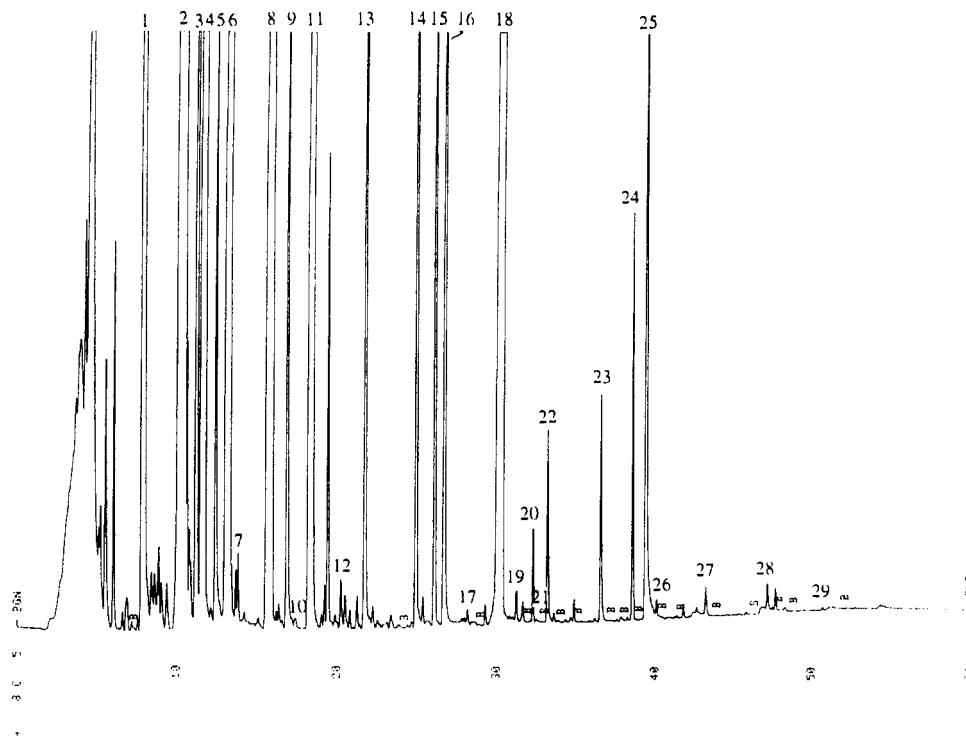
Figure 5. Chromatogram for a standard solution composed of the following: 1, isoamyl acetate; 2, limonene; 3, trans-2-hexenal; 4, ethyl hexanoate; 5, pentanol; 6, ethyl pyruvate; 7, hexyl acetate; 8, ethyl heptanoate; 9, hexanol; 10, ethyl lactate; 11, methyl octanoate (IS); 12, trans-2-hexen-1-ol; 13, heptanol; 14, benzaldehyde; 15, linalool; 16, octanol; 17, butanoic acid; 18, cis-3-hexen-1-ol; 19, γ-butyrolactone; 20, diethyl succinate; 21, citronellol; 22, α-terpineol; 23, ethyl decanoate; 24, 2-phenethyl acetate; 25, ethyl laurate; 26, hexanoic acid; 27, benzyl alcohol; 28, heptanoic acid; 29, octanoic acid.

rate of 67 mL/min). From this the V_r was calculated to be 2010 mL.

To understand whether different concentrations of a compound remain within the linearity zone or in the saturation zone, four solutions of 12, 6, 4, and 3 ppm, each containing limonene, benzaldehyde, 2-phenethyl acetate, and octanoic acid, were adsorbed using adsorption times of 10, 20, and 40 min for the flow rate indicated. In all cases the variation coefficients were in the order of 3% (n = 3), although less for the octanoic acid (12%). Figure 4 shows the graphs for the above compounds. Octanoic acid was not detectable after 10 min of adsorption in the solutions of 3 and 4 ppm. The rest of the compounds showed lineal increases of peak areas when the time was increased, except limonene in the 12 ppm solution after 20 min of adsorption.

The graphs of compound area/internal standard against concentration for each of the adsorption times gave calibrations with correlation coefficients greater than 0.99 and significance levels lower than 0.1% for all of the compounds, except limonene at 40 min and octanoic acid at 10 min.

On the basis of the above results, a time of 20 min was chosen as the most suitable for purposes of this study, although this is slightly superior to V_s defined, since the heavy fraction compounds of wine aromas seldom exceed 6 ppm and there should be no risk of saturating the Tenax. By using the 20-min time, smaller peak areas were more easily detectable.

Figure 5 shows a chromatogram obtained from a new standard solution using the mentioned compounds and 20 min of adsorption time. Calibration was carried out with standard solutions of 1.5, 3, and 6 ppm, and lineal correlations exceeding 0.96 and significance levels below 0.1% were obtained for all compounds except octanoic acid, which could not be detected in the 1.5 ppm solution. The variation coefficients were 3–5 % for n = 3 in all
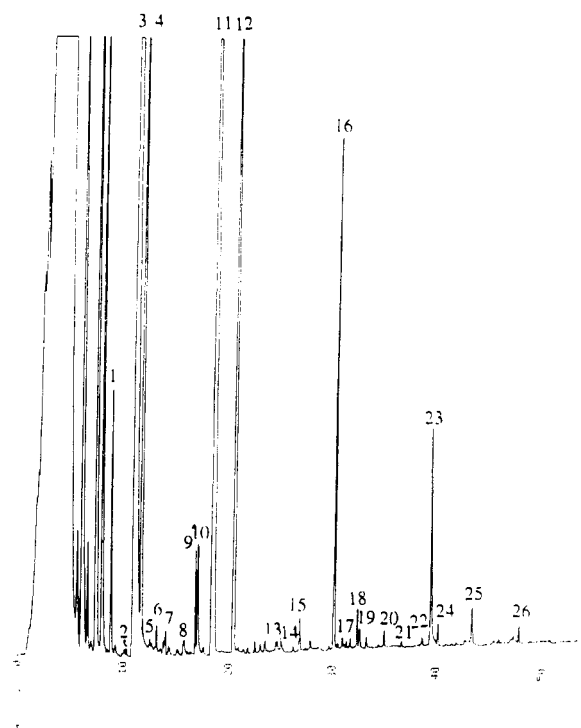

Figure 6. Chromatogram for a wine whose compounds and their concentrations are (in ppm) as follows: 1, isoamyl acetate (1.82); 2, limonene (0.39); 3, trans-2-hexenal (5.02); 4, ethyl hexanoate (0.55); 5, pentanol (0.13); 6, ethyl pyruvate (0.14); 7, hexyl acetate (1.27); 8, ethyl heptanoate (2.24); 9, hexanol (0.72); 10, ethyl lactate (0.96); 11, methyl octanoate (IS); 12, trans-2-hexen-1-ol (12.00); 13, benzaldehyde (0.37); 14, linalool (1.56); 15, octanol (0.13); 16, cis-3-hexen-1-ol (0.15); 17, γ-butyrolactone (1.70); 18, diethyl succinate (2.30); 19, citronellol (1.73); 20, α-terpineol (0.24); 21, ethyl decanoate (0.12); 22, 2-phenethyl acetate (0.17); 23, ethyl laurate (0.36); 24, hexanoic acid (0.96); 25, benzyl alcohol (3.59); 26, heptanoic acid (1.40).

compounds except octanoic acid, for which it was 9%. Application of these results to a characteristic wine of the region (D. O. La Mancha) is show in Figure 6, in which the compounds and their determined concentrations can be seen.

Therefore, this method is proposed as a rapid technique not involving sample manipulation for determining the volatiles of the heavy fraction of wine aromas.

ACKNOWLEDGMENT

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