A Comparative Study of the Ability of Different Solvents and Adsorbents to Extract Aroma Compounds from Alcoholic Beverages

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Abstract

Seven liquid solvent systems—dichloromethane, dichloromethane–pentane (1:1), freon 113, diethyl ether–pentane (1:1 and 1:9), ethyl acetate–pentane (with and without an additional salting-out effect) (1:3 and 1:20), and seven solid-phase extraction (SPE) systems (Amberlite XAD-2, 4, 7, and 16; Porapak Q; C8; and C18)—are comparatively studied. The distribution coefficients between the extraction system and a hydroalcoholic solution (12% v/v in ethanol, pH = 3.2) of 14 selected volatile compounds belonging to different chemical families and polarities are calculated. The results are processed by factor analysis and cluster analysis, and the following conclusions are reached. First, the efficiency of extraction decreases in this order: polymeric sorbents > silica-based sorbents > liquid–liquid systems with salting-out effect ≈ dichloromethane > rest of liquid solvents. Second, the addition of salt mainly increases the recovery of compounds with Lewis acid properties. Third, the efficiency of the extraction of a liquid solvent depends not only on its polarity but also on its solubility in water. Fourth, in regards to the selectivity of the SPE systems, Porapak Q is the best to extract nonpolar compounds, Amberlite XAD 4 and 16 provide the least selective extraction profiles, and C8 and C18 have a special ability to extract compounds with a Brønstedt–Lowry character. Results indicate that in all cases liquid solvents can be replaced satisfactorily by SPE systems.

Introduction

Alcoholic beverages can contain more than 1300 volatile compounds, some of which are important analytical objectives because of different reasons such as their aromatic properties (1–8), their possible use as markers of origin (9–12), and the fact that some of them can be detrimental to the sensory quality of the product (13). Although all the volatile molecules tend to be small and not very polar components, a large part of chemical families and consequently chemical and physical properties are represented in the volatile fraction of an alcoholic beverage (2,14). A second and main characteristic of the analysis of volatile compounds in alcoholic beverages is the fact that they contain ethyl alcohol and several other major fermentation compounds, which will complicate the isolation of volatile compounds. The presence of alcohol has a deep effect on the extraction abilities of the different solvent and adsorbent systems. The solubilities of solvents are higher than those found in the case of water, and in both cases, the extraction coefficients are significantly lower than those found in the case of water because of the higher solubilities of most of the volatile compounds in hydroalcoholic systems. In addition, most of the alcoholic beverages contain important amounts of several other metabolites from the alcoholic fermentation. These are the so-called fusel alcohols (isobutyl, 2- and 3-methylbutyl, and β-phenylethyl alcohols), several polyols, and in some cases ethyl esters of several organic acids (ethyl lactate and ethyl succinate) (2,14). Unfortunately, most of these compounds are easily extractable, thus almost any organic extract obtained from an alcoholic beverage is mainly composed of them. This seriously limits the detection limits that can be reached in a normal high-resolution gas chromatographic operation and introduces several difficulties in the analysis of ultratrace analytes.

Leaving aside the dynamic headspace concentrations and the most recent solid-phase microextractions, the most common solution has involved the use of liquid–liquid extractions with various selected solvent systems. The most efficient systems have been continuous extractions with freon-11 (15,16), dichloromethane (17), or several azeotropic mixtures (18). Some of these (particularly freon-11) worked reasonably well and made it possible to get high-quality (i.e., clean and concentrated) extracts. However, there is an increasing concern about the use of a high amount of solvents that can harm the ozone layer or that are toxic, carcinogenic, or explosive (and in any case increasingly expensive). Several authors have studied the use of different solid-phase extraction (SPE)

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systems, and in some cases, they have been successful in the development of analytical methods (19–22). However, no systematic studies have been carried out that compares the performance of the different liquid–liquid or solid–liquid extraction systems, which would be of particular help in method development. The main aims of this study were to compare the extraction abilities of different solvent and adsorbent systems in hydroalcoholic media and provide data that might allow the selection of one of these systems according to quantitative criteria.

Experimental

Absolute ethanol P.A. was obtained from Riedel-de Häen (Seelze, Germany); freon 113 (1,1,2-trichlorotrifluoroethane, HPLC-grade) from Merck (Darmstadt, Germany); dichloromethane, acetonitrile, and hexane (HPLC-quality) from Fisher Scientific (Loughborough, UK); diethyl ether P.A. from Fluka (Buchs, Switzerland); ethyl acetate (HPLC-grade) and acetone P.A. from Panreac (Barcelona, Spain); methanol (HPLC-grade) from LAB-SCAN (Dublin, Ireland); and pentane (95% pestipur) from SDS (Peypin, France).

Water was obtained from a Milli-Q purification system (Millipore, Bedford, MA).

Solid sorbents

Octyl-functionalized silica gel (C8) and octadecyl-functionalized silica gel (C18) were obtained from Aldrich (Steinhein, Germany); Amberlite (XAD-2, XAD-4, XAD-7, and XAD-16) from Supelco (Madrid, Spain); and Porapak-Q from Supelco (Madrid, Spain).

Chemical standards

The following chemical standards used in this study were 99.5% ethyl pentanoate (PolyScience, Niles, IL); 99.0% isoamilic alcohol (Aldrich); acetic acid (Panreac, Glacial, PA); 99.0% 2-isobutyl-3-methoxypyrazine (Aldrich); 98.0% linalool (Aldrich); 99.5% ethyl decanoate (PolyScience); 99.0% isovaleric acid (Aldrich); 99.5% geraniol (Fluka); 98.0% guaiacol (Aldrich); 99.0% 2-phenylethyl alcohol (Fluka); 98.0% β-ionone (Sigma); 97.0% γ-nonalactone (Aldrich); 99.0% eugenol (Aldrich); and 98.0% 4- and 5-dimethyl-3-hydroxy-2,5-dihidrofuran-2-one (sotolon) (Aldrich).

The internal standard solution was 2-octanol in ethanol (1 µg/mL).

The Hydroalcoholic solution conditions were 12% v/v in ethanol, 5 g/L tartaric acid, pH adjusted to 3.2 with NaOH, and 1M containing 10 mg/L of the selected volatile compounds.

Determination of distribution coefficients of liquid–liquid systems

All the determinations were performed in 15-mL screw-capped centrifuge tubes. A volume (10 or 5 mL) of hydroalcoholic solution containing 10 mg/L of each of the selected volatiles was added and extracted with 1 or 0.5 mL of the solvent. The tube was shaken for 45 min and then centrifuged at 2500 rpm for 5 min. The organic extract was recovered, spiked with 20 µL of the internal standard solution, and analyzed by gas chromatography (GC). The areas of the analytes were divided by the area of the internal standard and interpolated in a calibration graph built through the analysis of organic solutions containing known amounts of analytes. All the determinations were carried out replicately on different days, and at least three phase ratios were assayed (1:20, 1:10, and 1:5).

In order to study the salting-out effect, 3.3 g of $(NH_4)_2SO_4$ was added to the extraction tube, and the volume of hydroalcoholic solution was limited to 7.9 or 3.95 mL to ensure a similar phase ratio. The rest of the process was similar to that explained previously.

Determination of distribution coefficients of solid–liquid systems (retention)

Solid sorbents were initially washed with methanol and dried under vacuum (25 mm until constant weight). An exact weight of the sorbent (approximately 0.50 g) was placed inside a 30-mL glass vial together with 5, 10, or 20 mL of a hydroalcoholic solution containing 10 mg/L of the selected volatiles. All the determinations were carried out replicately on different days, and at least three phase ratios were assayed (1:40, 1:20, and 1:10). The vials were shaken softly for 6 h. After this time, 7.9 mL of the hydroalcoholic solution was removed and added to a 15-mL centrifuge tube containing 3.3 g $(NH_4)_2SO_4$ together with 20 µL of the internal standard solution and 1 mL of dichloromethane. The tubes were closed and shaken gently for 45 min, centrifuged, and the organic phase was analyzed by GC. The areas obtained were divided by those of the internal standard and then interpolated in calibration graphs built by the analysis of hydroalcoholic solutions containing known amounts of volatile compounds.

Determination of distribution coefficients of solid-liquid systems (elution)

An exact weight of a previously conditioned XAD-4 sorbent (approximately 0.17 g) was placed inside a 4-mL glass vial together with 10 µL of a standard solution with the selected volatile compounds in ethanol (1000 µg/mL) and 1 mL of the organic solvent.

The two phases were in contact for approximately 10 h in order to reach equilibrium. After this time, an exact volume of the organic solvent (approximately 0.75 mL) was removed to a 2-mL glass vial together with 20 µL of the internal standard solution. The organic phase was analyzed by GC as explained previously.

GC

A Hewlett-Packard 5890 series II GC with a 50-m × 0.32-mm column (0.5-µm film thickness), Carbowax 20 M, from J&W Scientific (Folsom, CA) was used. The column was preceded by a 2-m × 0.53-mm uncoated precolumn. The temperature program was set to 40°C for 5 min and then raised at 5°C/min to 190°C. The carrier gas was H_2 at 3 mL/min. Other conditions included a splitless injection, a 120-s splitless time, a 30-mL/min flow, and a flame ionization detector.

Data analysis

All of the data analysis was carried out by the Statistical Package for the Social Sciences (SPSS) statistical software system, version 8.0.

Results and Discussion

Crude results are given in Tables I, II, and III. These Tables give the distribution coefficients (K) of a series of selected volatile compounds between a synthetic wine (12% ethanol, pH = 3.2) and the organic solvent or the solid adsorbent. These results were obtained using different phase ratios and in all cases after replicating analysis on different days. However, several of the confidence intervals were quite wide, because the extraction in some cases was almost total and the determination of both the extracted and remaining analyte carried a high imprecision. The K values given in the Tables were not corrected for the variations of the phase volumes. Instead, they referred to the initial volumes contacted, which is more practical and useful but slightly questionable from a theoretical point of view. In the case of the SPE systems, the K values given were the quotients between the mass of the analyte (after equilibrium) per mass unit of adsorbent added and the concentration of the analyte in the liquid phase. The compounds selected for the study represent different families of chemical compounds present in the volatile fraction of alcoholic bever-

Table I. Distribution Coefficients of Selected Analytes Between Several Solvents* and a 12% Hydroalcoholic Solution (v/v)

	D		D:P	1/1	F		E:P	1/1	E:P	1/9	EA:P	1/3	EA:P	5/95
Analyte	K		K		K		K		K		K		K	
Ethyl pentanoate	47	± 3	30	± 1	87	± 9	11	± 0	17	± 1	17	± 1	21	± 1
Isoamyl alcohol	5	± 0	3	± 0	0.7	± 0.1	0.8	± 0.1	0.5	± 0.1	0.7	± 0.1	0.4	± 0.1
Acetic acid	0	–	0	–	0	–	0	–	0	–	0.3	± 0.1	0	–
2-Methoxy-3-isobutylpirazine	100	± 11	41	± 2	70	± 5	12	± 0	20	± 1	21	± 1	27	± 1
Linalool	94	± 9	37	± 2	42	± 2	12	± 0	17	± 1	18	± 1	21	± 1
Ethyl decanoate	24	± 1	12	± 0	21	± 1	12	± 0	16	± 0	18	± 1	23	± 1
Isovaleric acid	3	± 0	1	± 0	0.3	± 0.1	1	± 0	0.4	± 0.1	0.5	± 0.1	0.2	± 0.1
Geraniol	3300	± 1300	61	± 4	41	± 2	13	± 0	16	± 0	16	± 0	18	± 1
Guaiacol	30	± 1	9	± 0	2	± 0	1	± 0	1	± 0	1	± 0	1	± 0
β-Phenylethyl alcohol	17	± 1	4	± 0	0.6	± 0.1	0.7	± 0.1	0.4	± 0.1	0.5	± 0.1	0.3	± 0.1
β-Ionone	44	± 2	30	± 1	57	± 4	12	± 0	20	± 1	19	± 1	25	± 1
γ-Nonalactone	161	± 27	48	± 3	22	± 1	6	± 0	6	± 0	8	± 0	7	± 0
Eugenol	161	± 27	40	± 2	23	± 1	9	± 0	10	± 0	11	± 0	12	± 0
Sotolon	2	± 0	0.5	± 0.1	0.04	± 0.10	0.05	± 0.10	0.02	± 0.10	0.02	± 0.10	0.01	± 0.10

* Dicloromethane, D; pentane, P; freon 113, F; diethyl ether, E; ethyl acetate, EA.

Table II. Distribution Coefficients of Selected Analytes Between Several Solvents* and a 12% Hydroalcoholic Solution (v/v) with a Salting-Out Effect

	D		D:P	1/1	F		E:P	1/1	E:P	1/9	EA:P	1/3	EA:P	5/95
Analyte	K		K		K		K		K		K		K	
Ethyl pentanoate	86	± 9	31	± 1	289	± 46	45	± 3	63	± 5	86	± 9	73	± 6
Isoamyl alcohol	95	± 10	32	± 1	19	± 1	53	± 3	14	± 0	48	± 3	62	± 4
Acetic acid	3	± 0	1	± 0	0	± 0	2	± 0	0	± 0	4	± 0	10	± 0
2-Methoxy-3-isobutylpirazine	149	± 25	36	± 2	226	± 57	65	± 5	84	± 8	105	± 12	101	± 11
Linalool	130	± 19	34	± 2	204	± 41	58	± 4	73	± 6	99	± 11	96	± 11
Ethyl decanoate	61	± 4	23	± 1	51	± 3	32	± 1	37	± 2	45	± 3	59	± 4
Isovaleric acid	120	± 16	42	± 2	19	± 1	91	± 9	12	± 0	60	± 4	101	± 11
Geraniol	241	± 60	37	± 2	773	± 173	48	± 3	84	± 8	185	± 37	160	± 27
Guaiacol	109	± 14	27	± 1	12	± 0	41	± 2	8	± 0	33	± 1	45	± 3
β-Phenylethyl alcohol	129	± 18	29	± 1	11	± 0	49	± 3	8	± 0	36	± 2	50	± 3
β-Ionone	38	± 2	17	± 1	15	± 0	14	± 0	14	± 0	22	± 1	20	± 1
γ-Nonalactone	119	± 15	31	± 1	85	± 8	68	± 5	44	± 3	75	± 6	75	± 6
Eugenol	107	± 12	29	± 1	64	± 5	65	± 5	40	± 2	63	± 5	66	± 5
Sotolon	67	± 5	14	± 0	1	± 0	6	± 0	0.4	± 0.1	4	± 0	8	± 0

* Dichloromethane, D; pentane, P; freon 113, F; diethyl ether, E; ethyl acetate, EA.

Table III. Distribution Coefficients of Selected Analytes Between a Solid Sorbent and a 12% Hydroalcoholic Solution (v/v)

	XAD-2		XAD-4		XAD-7		XAD-16		Por-Q		C8		C18	
Analyte	K		K		K		K		K		K		K	
Ethyl pentanoate	293	± 42	410	± 82	83	± 4	299	± 43	1105	± 353	395	± 79	259	± 32
Isoamyl alcohol	21	± 1	33	± 1	7	± 0	28	± 1	23	± 1	4	± 0	0	–
Acetic acid	0	–	2	± 0	0.2	± 0	0	–	0	–	27	± 1	23	± 1
2-Methoxy-3-isobutylpirazine	289	± 36	395	± 79	115	± 7	292	± 42	2748	± 1248	660	± 220	461	± 92
Linalool	270	± 34	399	± 80	138	± 10	291	± 42	2327	± 1034	161	± 14	87	± 4
Ethyl decanoate	1089	± 245	1018	± 209	1166	± 283	813	± 201	1200	–	281	± 40	305	± 44
Isovaleric acid	2	± 0	14	± 0	0	–	9	± 0	5	± 0	26	± 1	14	± 0
Geraniol	282	± 35	493	± 123	186	± 17	356	± 59	1230	± 315	3286	± 3286	1663	± 663
Guaiacol	55	± 2	114	± 7	30	± 1	89	± 5	73	± 3	258	± 32	124	± 8
β-Phenylethyl alcohol	48	± 2	103	± 6	22	± 1	82	± 4	69	± 3	0	–	0	–
β-Ionone	655	± 118	1020	± 310	507	± 127	662	± 221	1050	–	1050	–	1050	–
γ-Nonalactone	255	± 32	451	± 90	127	± 9	287	± 41	1372	± 386	283	± 41	125	± 8
Eugenol	236	± 26	420	± 84	151	± 12	281	± 40	1719	± 619	58	± 2	19	± 1
Sotolon	6	± 0	14	± 0	6	± 0	10	± 0	7	± 0	0	–	0	–

Table IVA. Physical Properties of Solvents*

	D	E	EA	P	ET	F
Molecular weight	84.93	74.12	88.11	72.15	46.07	187.38
Density (g/mL)	1.326	0.7133	0.9006	0.6262	0.7893	1.57
Viscosity (cP)	0.44	0.24	0.45	0.23	1.194	n/a
Solubility in water (%)	1.6	6.89	8.7	0.04	100	n/a
Water solubility in solvent (%)	0.24	1.26	3.3	0.009	100	n/a
Boiling point (°C)	39.75	34.55	77.11	36.07	78.0	n/a
Dipole moment	1.6	1.15	1.78	0	1.69	n/a
Surface tension (dyn/cm)	28.16	17.1	23.75	16	22.8	n/a
Solvent strengh parameter (P')	3.1	2.8	4.4	0	–	n/a

* Dichloromethane, D; diethyl ether, E; ethyl acetate, EA; pentane, P; ethanol, ET; freon 113, F.

ages and thus represent a wide range of physico-chemical properties that cover almost all types of possible analytical objectives. Finally, Table IV gives data about the solvents and adsorbents that are useful to interpret the results.

In order to interpret the results more easily, a principal component analysis was carried out on the data set. The original matrix was composed of 14 rows (the 14 different analytes) and 21 columns (the 21 extraction systems studied). In this analysis, we used the logarithms of the K values instead of the correlation coefficients, which have allowed us to obtain a better representation of the samples in the factorial space. Three factors were finally selected retaining 92.3% of the original

Table IVB. Physical Properties of Sorbents

	XAD-2	XAD-4	XAD-7	XAD-16	Porapak-Q	C8	C18
Chemical nature	Hydrophobic styrene-divinylbenzene copolymer	Hydrophobic styrene-divinilbenzene copolymer	Hydrophilic structure based on metacrylate polymer	Polyaromatic	Hydrophobic ethylvinylbenzene-divinylbenzene copolymer	Octyl-functionalized silica gel	Octadecyl-functionalized silica gel
Pore volume (mL/g)	0.65	0.92	1.14	1.82	n/a	0.74–0.84	0.74–0.84
True wet density (g/mL)	1.02	1.02	1.05	1.02	n/a	n/a	n/a
Skeletal density (g/mL)	1.08	1.08	1.24	1.08	0.34	n/a	n/a
Mean surface area (m^2/g)	300	725	450	800	500–600	480–540	480–540
Mean pore diameter (A)	90	40	90	100	75	60	60
Mesh size	20–60	20–60	20–60	20–60	80–100	230–400	230–400

variance (62.5 being the first, 17.6 the second, and 12.2 the third). Therefore, the principal component representation displays the whole data set fairly well.

Table V shows the factor loadings used to express each variable as a function of the three factors (that is, the correlation coefficients between the factors and the variables). Figures 1A and 1B show the representation of these factor loadings in the two planes F1–F2 and F1–F3. As can be seen, γ-nonalactone, linalool, 2-methoxy-3-isobutylpyrazine, guaiacol, eugenol ethyl valerate, ethyl decanoate, and geraniol were mainly correlated with the first factor and acetic acid with the third one. The rest of the compounds were not correlated with a single factor. The first factor can then be defined as the general measure of the ability of the system to extract organic compounds from water. In fact, all the compounds were positively correlated to this factor, but the highest correlation correspondents were correlated to the least polar components. Therefore, the higher the value of this factor, the higher is the ability of the system to extract the least polar volatile compounds from hydroalcoholic solutions. The second factor is correlated with those analytes that show a strong Lewis acid character (with the exception of acetic acid), and it is anticorrelated with the other analyte with the opposed character (β-ionone). Finally, the third factor is correlated with those analytes showing a Brønsted–Lowry acid character. Therefore, the higher the value of the second factor, the higher is the ability of the system to extract Lewis acids (isovaleric acid, β-phenylethyl alcohol,

Table V. Principal Component Analysis and Factor Loadings

Analyte	Factor 1	Factor 2	Factor 3
γ-Nonalactone	0.983	–0.09055	–0.03695
Linalool	0.932	–0.306	0.08181
2-Methoxy-3-isobutylpirazine	0.927	–0.128	–0.213
Guaiacol	0.914	0.06620	0.327
Eugenol	0.908	0.04763	–0.373
Ethyl pentanoate	0.900	–0.315	0.02289
Ethyl decanoate	0.825	–0.379	–0.165
Geraniol	0.809	–0.269	0.237
Sotolon	0.755	0.582	–0.150
β-Ionone	0.709	–0.628	–0.01737
Isoamyl alcohol	0.653	0.712	–0.121
β-Phenylethyl alcohol	0.618	0.655	–0.404
Isovaleric acid	0.516	0.591	0.564
Acetic acid	0.317	0.104	0.896

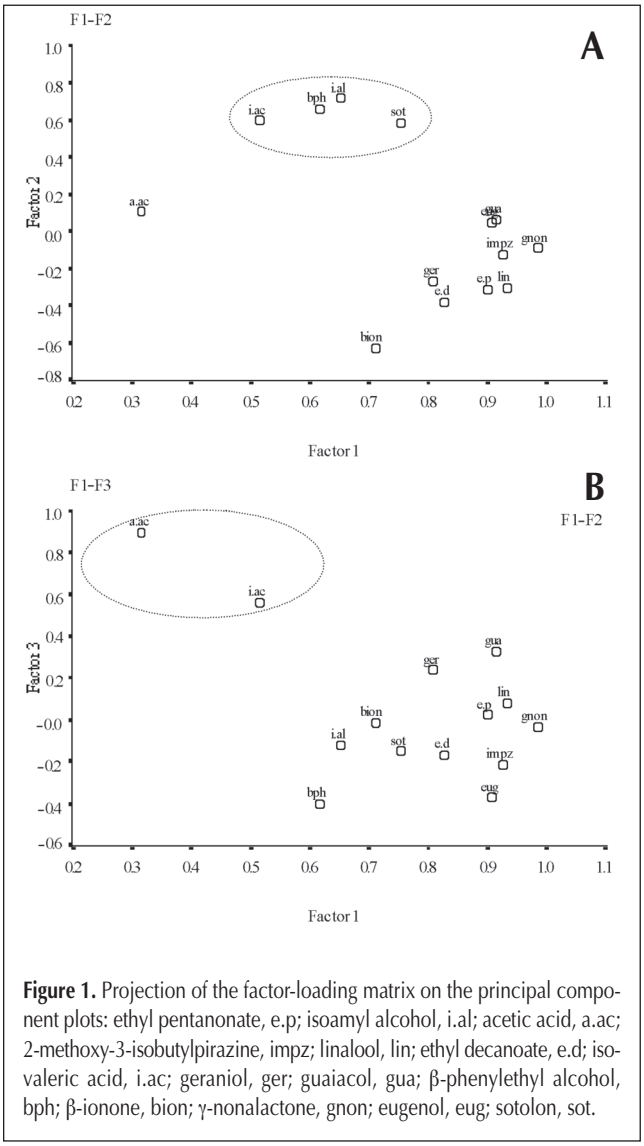

Figure 1. Projection of the factor-loading matrix on the principal component plots: ethyl pentanonate, e.p; isoamyl alcohol, i.al; acetic acid, a.ac; 2-methoxy-3-isobutylpirazine, impz; linalool, lin; ethyl decanoate, e.d; isovaleric acid, i.ac; geraniol, ger; guaiacol, gua; β-phenylethyl alcohol, bph; β-ionone, bion; γ-nonalactone, gnon; eugenol, eug; sotolon, sot.

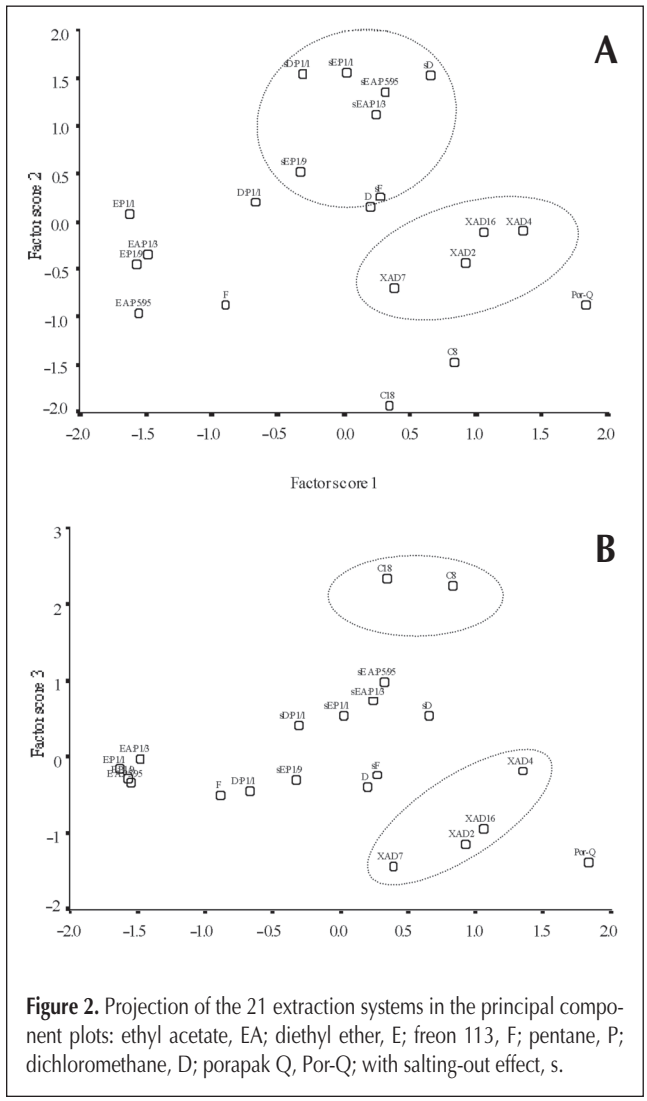

Figure 2. Projection of the 21 extraction systems in the principal component plots: ethyl acetate, EA; diethyl ether, E; freon 113, F; pentane, P; dichloromethane, D; porapak Q, Por-Q; with salting-out effect, s.

isoamyl alcohol, and sotolon), and the higher the value of the third factor, the higher is the ability of the system to extract Brønsted–Lowry acids (acetic acid and isovaleric acid).

The graphic representation of the 21 extraction systems considered in this study on the planes formed by the three factors can be seen in Figures 2A and 2B. Figure 2A clearly shows that all the SPE systems lie at the bottom-right part of the planes formed by the two first factors, very well-separated from the rest of the extracting systems. The liquid solvent systems without salting-out effects are grouped on the left part of the plane (with the exception of the two systems composed of dichloromethane), and the liquid solvent systems with salting-out effects are grouped on the central-upper part of the plane (except freon 113 and the system composed of a 9:1 pentane–ether mixture). Figure 2B only added that silica-based systems (C8 and C18) were very different from the rest of the solid adsorbents, because the former had the highest score in the third factor.

This set of results allows us to make the following observations and comments:

(*a*) First, the general ability of the different systems to extract volatile compounds from hydroalcoholic solutions decreased following the order indicated thus: polymeric sorbents > silica-based sorbents ≥ liquid solvents with salt ≈ dichloromethane >> liquid solvents. The actual advantage of the SPE systems over the liquid–liquid systems could be questioned, because the values for the former did not take into account the need to elute or re-extract the compounds sorbed. In order to solve this question, the K values of the test analytes between the solid sorbent and different solvents were calculated. These results (referred to as Amberlite XAD-4 resins) are given in Table VI and clearly show that the elution with two to three volumes of dichloromethane, diethyl ether–pentane, or acetone will be enough to recover most of the analytes quantitatively. Because in normal practice, sorbents are used packed in columns with several plates (between 2 and 10), the advantage of SPE systems over liquid–liquid systems is still clearer.

(*b*) Second, the addition of salt to the liquid–liquid systems had two effects: on the one hand (as was stated previously), it increased the general extraction ability of the systems, and on the other hand, it mainly increased the extraction ability of substances with Lewis acid characteristics. This result is not surprising, because the more ionic the media, the lower is the solubility of all neutral molecules in water; and the higher the solubility in water of the molecule (noting that Lewis acids are more soluble in water), the bigger is the decrease.

(*c*) Third, when considering only the liquid solvent systems (without salt), it can be seen that the general extraction ability decreased in the following order: dichloromethane > dichloromethane–pentane > freon 113 > ethyl acetate–pentane and diethyl ether–pentane systems.

It must also be observed that the effect of increasing the amount of active solvent in the ethyl acetate and diethyl ether systems also increased the ability to extract compounds with Lewis acid character, and in the dichloromethane system, the effect was the increase of the general extraction ability. These results suggest that the extraction ability of a solvent depends not only on its polarity, but also on its solubility in water. Although the ether–pentane and ethyl acetate–pentane mixtures can have polarities similar to dichloromethane or freon 113, they are less efficient because they are more soluble in water (see Table IV).

(*d*) Fourth, in regards to the SPE systems, it can be seen that silica-based sorbents had a special selectivity towards those compounds with Brønstedt–Lowry properties. Porapak Q provided the highest extraction efficiencies for nonpolar compounds (Amberlite XAD-4 and 16 had a slightly less general extraction efficiency, but a higher recovery of Lewis acids). Finally, Amberlite XAD-2 and 7 (C8 and C18) were the weakest sorbents. A short look at Table IV clearly indicates that general efficiency is partly related to the sorbent-specific surface.

A comparison between the extraction profiles of the different extraction systems can be seen in Figure 3. This figure represents the dendrogram obtained in the cluster analysis of

Table VI. Distribution Coefficients of Selected Analytes Between a Solvent and a Solid Sorbent*

	D		H		E		H–E	(1/9)	D–H	(1/1)	M		A		AN	
Analyte	**K**		**K**		**K**		**K**		**K**		**K**		**K**		**K**	
Ethyl pentanoate	0	–	0.157	± 0.104	0.024	± 0.011	0	–	0	–	1.419	± 0.095	0	–	0.049	± 0.269
Isoamyl alcohol	0	–	0.160	± 0.090	0	–	0	–	0	–	0	–	0.073	± 0.083	0.416	± 0.080
Acetic acid	3.336	± 0.132	2.974	± 0.123	5.269	± 0.162	5.070	± 0.162	2.118	± 0.116	0	–	1.500	± 0.095	1.194	± 0.089
2-Methoxy-3-isobutylpirazine	0	–	0.984	± 0.099	0.168	± 0.168	0.144	± 0.072	0	–	2.991	± 0.118	0.155	± 0.078	1.378	± 0.093
Linalool	0	–	0.556	± 0.093	0.131	± 0.558	0.024	± 0.091	0	–	0.443	± 0.087	0.167	± 0.095	0.671	± 0.083
Ethyl decanoate	0	–	0.774	± 0.095	0.270	± 0.086	0.314	± 0.094	0	–	6.706	± 0.192	0.513	± 0.084	2.018	± 0.099
Isovaleric acid	0.746	± 0.099	1.579	± 0.104	1.620	± 0.103	1.500	± 0.107	0.343	± 0.095	0	–	0.255	± 0.081	0.507	± 0.081
Geraniol	0.034	± 0.040	1.569	± 0.104	0.515	± 0.089	0.512	± 0.096	0	–	3.015	± 0.118	0.611	± 0.085	1.550	± 0.093
Guaiacol	0	–	0.311	± 0.090	0.051	± 0.025	0	–	0	–	0.520	± 0.100	0.029	± 0.018	0.332	± 0.080
b-Phenylethyl alcohol	0.135	± 0.094	2.020	± 0.109	0.621	± 0.090	0.639	± 0.097	0.144	± 0.093	0.824	± 0.091	0.565	± 0.084	0.774	± 0.084
b-Ionone	0.154	± 0.097	1.801	± 0.107	0.625	± 0.090	0.659	± 0.098	0.042	± 0.093	4.375	± 0.141	0.951	± 0.088	2.159	± 0.101
g-Nonalactone	0	–	2.721	± 0.119	0.596	± 0.090	0.621	± 0.097	0	–	2.343	± 0.108	0.498	± 0.084	0.791	± 0.084
Eugenol	0.020	± 0.277	3.533	± 0.131	0.640	± 0.091	0.552	± 0.097	0.033	± 0.183	2.146	± 0.106	0.996	± 0.089	1.278	± 0.090
Sotolon	0.868	± 0.102	4.791	± 0.154	1.573	± 0.102	1.593	± 0.108	3.160	± 0.130	8.186	± 0.232	1.698	± 0.097	2.425	± 0.105

* Dichloromethane, D; hexane, H; diethyl ether, E; methanol, M; acetone, A; acetonitrile, AN.

the 21 extraction systems using the Pearson correlation coefficient as a disimilarity index. Within this representation, samples with the same selectivity were clustered together regardless of their extraction efficiency. The figure shows that the extraction systems fall into four broad selectivity groups. All the liquid–liquid systems without salt (with the exception of dichloromethane) together with Porapak Q resins and the diethylether–pentane (1:9) system had in common an extraction profile characterized by a very poor recovery of all the polar compounds (isoamyl alcohol, acetic acid, furfural, isovaleric acid, β-phenylethanol, and sotolon). The Amberlite XAD resins formed a second selectivity group. All of them had in common fairly good recoveries for all the compounds with the exception of acetic acid, isovaleric acid, and sotolon. The third group (formed by the two silica-based sorbents and by dichloromethane and freon-113 with salt) and the group finally formed by the liquid solvents with salt were the groups that had the most uniform (least selective) profile.

In conclusion, it can be said that SPE systems can provide far better extracts for the analysis of volatile compounds present in hydroalcoholic solutions than those provided by normal liquid–liquid systems. Although the extraction ability of liquid systems can be increased by the addition of salt, this concomitantly involves an increase in the amounts of major compounds (fusel alcohols) extracted, which as a consequence has an extract more difficult to analyze. Porapak Q resins are especially attractive to obtain clean extracts with very good recoveries. Amberlite XAD-4 and 16 are not that efficient, but are better to extract polar compounds. Silica-based sorbents are still less efficient, but provide a unique selectivity. The best liquid extraction systems are dichloromethane and freon-113 with salt. If they have to be replaced, the best choices are any of the SPE systems or the diethyl ether–pentane (1:9) system with salt.

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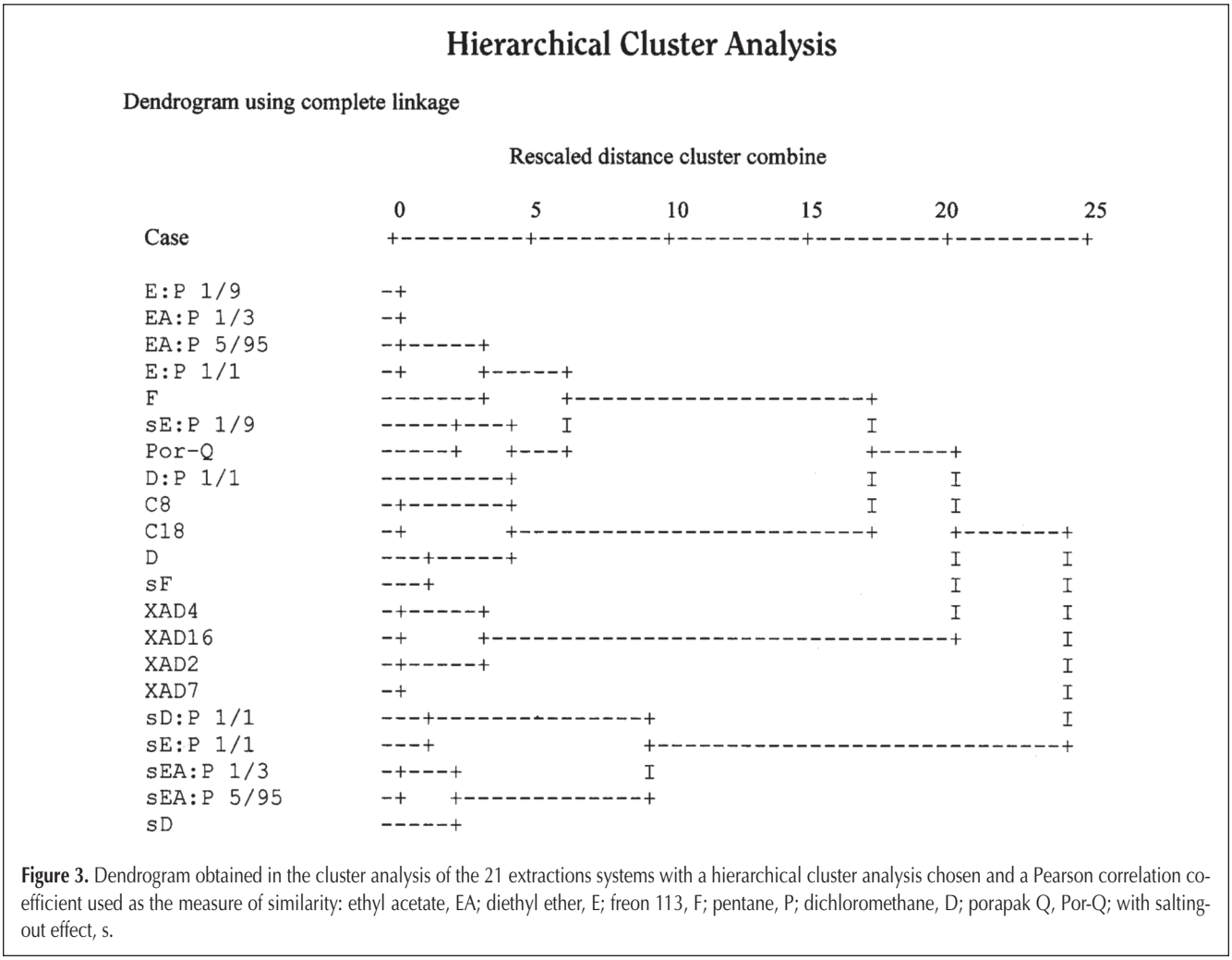

Figure 3. Dendrogram obtained in the cluster analysis of the 21 extractions systems with a hierarchical cluster analysis chosen and a Pearson correlation coefficient used as the measure of similarity: ethyl acetate, EA; diethyl ether, E; freon 113, F; pentane, P; dichloromethane, D; porapak Q, Por-Q; with salting-out effect, s.

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