Influence of Ethanol on Pesticide Extraction in Aqueous Solutions by Solid-Phase Microextraction

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The new extraction method, so-called solid-phase microextraction (SPME), coupled with gas chromatography-mass spectroscopy (GC-MS), was examined for the determination of residues of insecticides and fungicides commonly used for vineyard protection. Aqueous solutions containing between 0 and 15% ethanol were spiked with 12 selected compounds and diphenylamine at the level of 20 ppb (v/w), extracted onto a silica fiber coated with a 100-μm thickness of poly(dimethylsiloxane), and desorbed in the chromatograph injector. The influence of ethanol on the partition equilibrium between the adsorbant and the liquid was studied for each product. In several cases, equilibria were obtained, and the extracted amounts of pesticides were shown to be dependent on the nature of the molecule and on the ethanolic content of the solution. In contrast, the time necessary to reach these equilibria was the same in the presence and absence of ethanol. Additional experiments on natural wines spiked at the same level of concentration were analyzed under the same conditions, and the results were compared with those obtained from reference solutions.

Keywords: *Pesticide residues; wine; solid-phase microextraction (SPME); ethanol influence*

INTRODUCTION

Determination of pesticide traces in water has been optimized in recent years, especially since important developments of chromatographic techniques were introduced (HPLC, GC-MS, etc.). Sample preparation is actually the critical step for most analyses because usual methods based on liquid/liquid extraction (LLE) or on solid phase extraction (SPE), are not often totally efficient or sensitive enough to allow detection of analytes at low level. Recently, solid-phase microextraction (SPME) has been introduced by Pawliszyn and his group (Arthur and Pawliszyn, 1990; Arthur et al., 1992a,b; Potter and Pawliszyn, 1992; Louch et al.,1992), and application techniques are now in full development (Arthur et al., 1992c,d; Potter and Pawliszyn, 1994). The SPME method consists mainly of adsorbing analytes from aqueous solutions onto a fused silica fiber coated with a polymeric adsorbant. Partitioning of organics in the sample occurs between the aqueous phase and the polymeric adsorbant. Extracted compounds are then thermally desorbed in the injector of a gas chromatographic (GC) system and subsequently analyzed. Thus, this technique constitutes a convenient alternative to other commonly used extraction methods (purge and trap, liquid and solid phase extractions, etc.) because sampling can be done rapidly, directly, and without any solvent (Gorecki and Pawliszyn, 1995).

A convenient device is now commercially available from Supelco Company (Bellefonte, PA), making this technique simple and inexpensive. In the field of pesticide residue control, several studies have been published (Eisert et al., 1994; Popp et al., 1994; Barnabas et al., 1995; Eisert and Levsen, 1995a), showing mainly that triazines and organophosphorus herbicides can be easily traced by SPME in water or in soil solutions. Very recently, this work has been extended to other pesticides (Eisert and Levsen, 1995b), and the SPME method was validated with respect to the limit of detection, linearity, and precision.

Magdic and Pawlizyn (1996) extracted organochlorine pesticides from water and applied the SPME method to river and lake samples. In another recent publication, Boyd-Boland and Pawliszyn (1995) optimized a method allowing analysis of 22 nitrogen-containing herbicides in water and compared results from two different polymeric fibers (polar and nonpolar) and with different chromatographic detectors. The SPME method has even been applied to wine analysis, and some of these herbicides have been detected in commercial products.

Even if the use of the standard addition method makes this result in wine perfectly credible, it seemed interesting to look at the influence of alcohol in such an extraction method. It is assumed that ethanol, which is one of the major constituent of wines, can induce some variations of the partition coefficient of the organic pesticide compounds between the polymeric stationary phase and the aqueous solution in the SPME extraction. To justify the use of water samples spiked with methanol solutions of triazine standards in describing a determination method for organophosphorus pesticides, Eisert and Levsen (1995a,b) have already noticed that the presence of 20% of methanol reduced the peak response by a factor of about two, thus confirming the study by Arthur et al. (1992d) about the effect of methanol concentration on extractions of substituted benzene compounds by SPME.

Despite these recent observations concerning compounds that are not generally found in wines, the effect of a polar molecule such as ethanol, at a concentration that must be considered as a cosolvent of the pesticide residues, has not been investigated in detail. Moreover, methanol cannot be considered as a good model for ethanol in wine components because only traces can be found in natural wines and because its chemical properties can generate anomalous solvent effects caused by strong hydrogen bonding with water compared with higher alcohols (Arthur et al., 1992c).

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The objective of this work was to examine the variations in the partitioning equilibrium between the stationary and the liquid phases induced by the addition of ethanol to the aqueous solution, during the SPME of 12 pesticides chosen from those currently or potentially used for vineyard protection (insecticides, fungicides, and acaricides). The results obtained from an ethanolic aqueous solution were compared with those from natural wines, all spiked with the same products at the same concentration, to appreciate if an alcoholic aqueous solution is a good model for pesticide analysis in wines.

MATERIALS AND METHODS

Choice of Pesticides. Twelve pesticides were selected in different chemical classes of products: procymidone and vinclozolin (dicarboxyimide), folpet (phtalimide), triadimenol and Flusilazole (triazole), metalaxyl (acylamid), and dichlofluanid (sulfamid) as fungicides; parathion-methyl and phosalone (organophosphorothioate), and lindane and dieldrin (chlorohydrocarbon) as insecticides; and bromopropylate (benzylate) as an acaricide. Diphenylamine (DPA), which does have pesticidal properties but which is not used on vineyards, was added as an extraction standard for wine analysis. All pure-grade samples were purchased from Alltech France.

Stock solutions were initially prepared by dissolving pure pesticide in ethyl acetate at the concentration of 1 g/L and then diluting to 50 μg/mL with the same solvent. Stock alcoholic solutions of analyzed pesticides at the concentration of 20 μg/L (20 ppb, w/v) were prepared freshly every week from this solution by dilution with the calculated proportions of distilled water and pharmaceutical grade 95% aqueous ethanol.

Alcoholic concentrations of commercial wines were measured according to the usual method (OIV, 1990) and were arbitrarily reduced for standardization at 10% by dilution with the calculated amount of distilled water (wine A). A 10% alcoholic wine spiked sample (wine B) was prepared by adding 20 μg/L (w/v) of the pesticides to a wine A sample by the standard addition procedure. In this way, aqueous solutions and wine solutions never have >40 μL/L (40 ppm, v/v) of ethyl acetate. At such a concentration, ethyl acetate does not interfere in the extraction of these analytes.

Blank solutions were regularly tested to insure that no interferences were noticeable between eventual impurities and observed peaks in chromatograms.

SPME Procedure. The SPME device was purchased from Supelco France. Two fibers coated with poly(dimethylsiloxane) (PDMS) at both 30- and 100-μm thicknesses were used and compared. In the usual procedure, the syringe of the SPME device was introduced through a septum into a 4-mL sample vial where a 3-mL aliquot of the aqueous solution (or wine) was stirred at a regular speed of ≈200 rpm. The fiber was then drawn into the solution in such a way that it was just immersed into the liquid paraboloïd formed by the magnetic stirring. After the desired adsorption time was reached, the fiber was withdrawn into the syringe, which was removed from the vial and immediately introduced into the injection port of the GC.

SPME fibers were initially conditioned in a helium-swept injector at a temperature of 250 °C for 3 h and then repeatedly desorbed into the GC until a clear chromatogram was obtained. Blank desorbtions were also periodically run to ensure that no cumulative contaminations were interfering.

Chromatographic Analysis. The GC used was a Varian 3400 equipped with a Finnigan ITS 40 ion trap mass spectrometric (MS) detector. Separations were obtained with a Supelco PTE 5 column (30 m × 0.32 mm) with a phase thickness of 0.25 μm. A split/splitless injector was used in the splitless mode during the first 3 min after introduction of the fiber and the split mode (100 mL/min of helium) after 3 min. The injector temperature was maintained at 250 °C. The carrier gas was helium C (99.999% pure) supplied by Air Liquid Company. The optimized temperature program was as follows: 50 °C for 3 min, increased at 30 °C/min to 155 °C, then at 1 °C/min to 175 °C, then at 5 °C/min to 225 °C, and then at 30 °C/min to 300 °C, and finally held at 300 °C for 4 min. The ion trap was held at 220 °C and the transfer line at 250 °C. The MS was tuned to FC 43 (perfluorotributylamine), and masses between 35 and 450 amu were scanned. The most abundant ion peak characteristic of the compound in the corresponding part of the chromatogram was systematically used for quantification for each product: diphenylamine, 169; lindane, 219; parathion-methyl, 263; vinclozolin, 212; dichlofluanid, 123; folpet, 260; metalaxyl, 160; triadimenol, 112; procymidone, 283; dieldrin, 79; flusilazole, 206; bromopropylate, 185; and phosalone, 182. To enhance method sensitivity toward metalaxyl and triadimenol, which give much less ionic current than other selected compounds (see Figure 1), accumulation of three specific ions for each product were used and improved detected signals: metalaxyl, 160+192+206; triadimenol, 112+128+168.

Using these conditions, the linearity of the response of the mass detector was tested by injecting in triplicate 1 μL of ethyl acetate solutions of the selected pesticides over the range 0.5−50 mg/L. Correlation analysis of the curves was good (r > 0.99) for all compounds.

RESULTS AND DISCUSSION

Identification. Retention times, mass spectra, and specific ions were initially characterized for each of the 12 pesticides and DPA by directly injecting 1 μL of an ethyl acetate solution containing 1 mg/L of each of the pure compounds. Then, 1 μL of a solution of the whole mixture in the same solvent at the concentration of 1 μg/mL (1 ppm, w/v) was injected under the same conditions. For comparison, an SPME was run for 30 min (arbitrarily chosen time) from an aqueous solution of the same products at the concentration of 100 ppb (w/v) with a 100-μm PDMS-coated fiber and analyzed according to the described procedure. The two resulting chromatograms are shown in Figure 1. Because of the presence of the fiber in the insert of the injector during desorption, slightly different retention times were observed, but all peaks were easily identified according to mass spectra.

Observed signals were much greater (total ionic current) for most of the compounds from the extracted 100-ppb aqueous solution than from the injected 1-ppm organic solution. Even for triadimenol (peak 8), experiments with specific ions (see Table 2) showed that the accumulation effect on the fiber (which was less efficient than for the other compounds) increased the observed signals. In fact, metalaxyl (peak 5) is the only product that did not show an effective accumulation effect with these sampling conditions.

Comparison of Fibers. A fiber coated with 30 μm of the same adsorbent phase was recently marketed, with a specification for semivolatile compounds and especially for pesticides (Supelco, 1995). A comparison was made between this new fiber and the 100-μm coated one. Both fibers were immersed for 30 min, in two aliquots of the same pesticide aqueous solution at the concentration of 20 ppb (w/v), and then desorbed according to the described procedure. The results, listed in Table 1, clearly indicate that the amount of pesticides extracted by the 30-μm coated fiber was between 2- and 8-fold less than the 100-μm coated one, but give no indication if the time necessary to reach equilibrium for each compound is different when using one fiber or the other. Additional observations showed no differences between the fibers with regard to conditioning blank desorptions before first usage and desorption efficiencies after 3 min in the GC injector at 250 °C. The 100-μm coated fiber was then selected to achieve the better sensitivity for analysis.

Accumulation Effect and Reproducibility. To estimate the accumulation effect for 70 min of the SPME

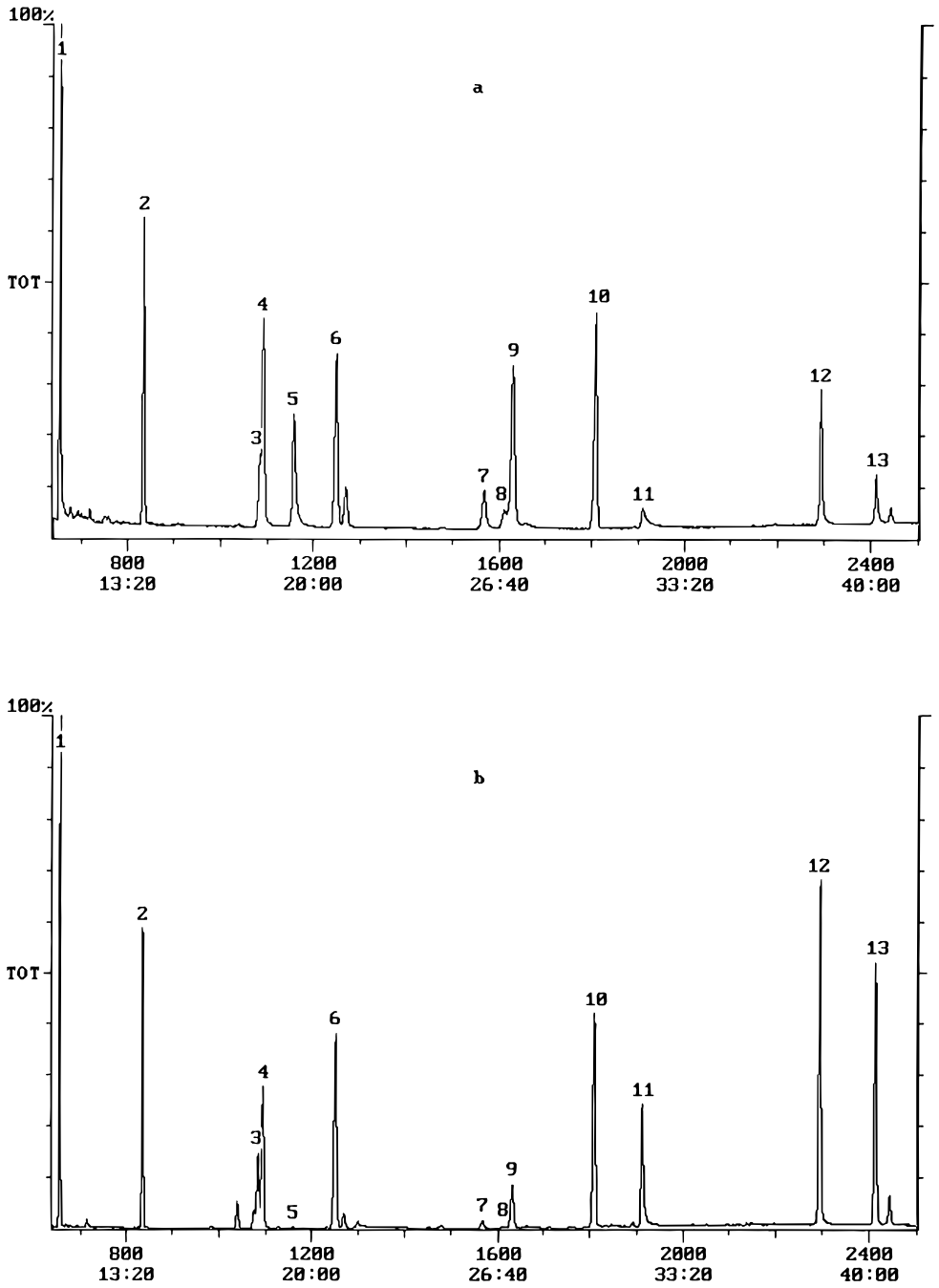

Figure 1. Gas chromatograms of the selected pesticides by (a) direct injection of 1 μL of an ethyl acetate solution at the concentration of 1 ppm and (b) SPME extraction for 30 min of 3 mL of a 100-ppb aqueous solution. Total ions detection. For component listing, see Table 1.

Table 1. Relative Efficiency of 100- and 30-μm PDMS-Coated Fibers in Extracting a 20 ppb Aqueous Solution by SPME for 30 min

compound	ratio of peak areas 100 μm/30 μm	compound	ratio of peak areas 100 μm/30 μm
DPA	4.3	triadimenol	5.5
lindane	4.7	procymidone	5.5
parathion-methyl	6.1	dieldrin	1.5
vinclozolin	4.7	flusilazole	8.6
metalaxyl	1.4	bromopropylate	1.5
dichlofluanid	5.0	phosalone	3.5
folpet	8.2		

method from a 20-ppb (w/v) solution of the selected pesticides in water compared with the direct injection method, seven replicates of the SPME extraction were performed with the described conditions and analyzed. The extracted amounts for each compound were calculated with the calibration obtained by the average response values from six replicates of the ethyl acetate solution injection (1 ng injected) and compared with the amounts contained in 1 μL of a solution of the same compounds at the same concentration (20 pg). The accumulation effect of the SPME method was thus exemplified, and the reproducibility of the method was tested from the same results presented in Table 2.

Important differences between accumulation effects from 0.5 (metalaxyl) to ≈300 (flusilazole, bromopropylate, and phosalone) were observed depending on the nature of the pesticide. In the case of flusilazole, for which the response coefficient is low, this accumulation effect was particularly because it allowed efficient detection by SPME at the level of 1 ppb and even below.

Table 2. Response Coefficient of the Ion Trap Detector for Each Analyte Directly Injected as a 1-ppm Ethyl Acetate Solution and Extracted by SPME from a 20-ppb Aqueous Solution (3-mL Aliquot)

			direct injection (1 ng)[a]		SPME (20 ppb/70 min)[b]			
no.	compound	specific ion	peak area (au)	RSD	peak area (au)	RSD	percent extracted (%)	accumulation effect[c]
1	DPA	169	119959	2.5	133319	4.0	1.8	54
2	lindane	219	37361	1.8	46155	7.2	2.1	63
3	parathion-methyl	263	20659	12.7	20775	8.5	1.7	51
4	vinclozolin	212	29904	1.5	31710	1.7	1.8	54
5	metalaxyl	160+192+206	95773	1.6	852	16.2	0.01	0.5
6	dichlofluanid	123	91873	1.5	162800	3.6	3.0	90
7	folpet	260	28565	3.5	3099	33.0	0.2	6
8	triadimenol	112+128+168	64779	11.8	1846	14.3	0.05	1.5
9	procymidone	283	38006	2.0	18343	5.5	0.8	24
10	dieldrin	79	177613	0.6	542541	24.7	5.1	153
11	flusilazole	206	7607	5.7	46892	14.0	10.3	309
12	bromopropylate	185	38140	3.4	242341	4.4	10.6	318
13	phosalone	182	38686	7.1	261555	14.0	11.3	339

[a] 1 μL of a solution at 1 mg/L; six replicates; au represents arbitrary units. [b] 100-μm PDMS-coated fiber; seven replicates. [c] Extracted amount by SPME/amount contained in 1 μL of the same solution (20 pg).

For triadimenol, the same effect was much less spectacular but gave a higher response compared with that from a direct 1-μL injection of a solution at the same concentration.

Relative standard deviations (RSD), expressed as a percentage of the mean value and calculated from the six replicates of the direct injection and from the seven replicates of the extraction, were slightly higher in the case of SPME extractions than in direct injections. The RSDs range from 2% for vinclozolin to 24% for dieldrin. The higher values are obtained for the late-eluting compounds and those that show a very small signal at this concentration (metalaxyl and triadimenol). The case of folpet, for which the RSD reaches 33%, is not representative because the molecule was found to decompose in water solution within a few hours (see next paragraph).

Ethanol Effect. Extractions of 0, 5, 10, and 15% alcoholic solutions of the 12 cited pesticides and DPA at the concentration of 20 ng/mL (20 ppb, w/v), which is a level currently examined in pesticide residue control for wines, were performed and analyzed in duplicate according to the described procedure. Detected signals, expressed in arbitrary units (ionic current), were plotted against adsorption times for each constituent of the mixture, and the 13 exposure−time profiles were divided into four models according to the shape of the curves (Figure 2): model a concerns vinclozolin (Figure 2a), DPA, lindane, parathion-methyl, dichlofluanid, procymidone, and phosalone; model b concerns bromopropylate (Figure 2b), dieldrin, and flusilazole; model c concerns triadimenol (Figure 2c) and metalaxyl; and model d concerns only folpet (Figure 2d). The behavior of this last compound is unique because it decomposes spontaneously in water at such a rate that extracted amounts at equilibrium decreased as exposure time increased.

How the equilibrium between the PDMS phase of the fiber and the aqueous solution is reached for each type of selected compounds is illustrated in Figure 2. It is clear that the equilibrium is dependant on both the nature of the analyte and the ethanolic concentration of the liquid phase. For 10 of the products (models a, c, and d), the equilibria were reached after ≈20 min or at least within the 70 min of the experiment (phosalone), and the time necessary to get a maximal extraction did not depend on the percentage of ethanol. In the three other cases, the equilibrium is not reached within the experimental duration but the extracted amount of residue is still alcoholic concentration dependent. Thus, an exposure time of the fiber in the analyte solution could not be absolutely determined for a typical analysis of all these pesticides because it would have been better to have a complete equilibrium for each extraction; nevertheless 30 min appeared as a possible compromise, as long as it is precisely measured, because it is a convenient chromatogram acquisition time.

In contrast the influence of ethanol content was significant for the amounts of analytes extracted for each exposure time. In all cases, the extraction efficiencies decreased when ethanol was present in the solution. The reduction varied according to each product, but the variation was much more important between 0 and 5% than between 5% and the other concentrations. For example, the decrease became dramatic in the cases of metalaxyl and triadimenol (model c), for which no signals could be detected as soon as ethanol concentration reached 10%, even for an exposure time of 70 min, whereas the signal was of the third level of magnitude for both compounds in the pure water solution. A third product, flusilazole, was strongly affected (two orders of magnitude in the same conditions) by the presence of ethanol, but the extracted amounts were approximately the same when the alcoholic percentage was between 5 and 15%.

Arthur and Pawliszyn (1990) have shown that the general phenomena applied in the SPME technique could be described, at the equilibrium, by the expression

$$K = C_s/C_l = M_s/M_l \times V_l/V_s \qquad (1)$$

where M_s and M_l are the amounts of analytes in the stationary phase and in the liquid, respectively, V_s and V_l are the volumes of these media, respectively (which were constant over the described experiments), and K is the partitioning coefficient for each product analyzed at the experimental temperature (room temperature). Considering that each analyzed 3-mL aliquot contained 60 ng of every product and that the V_s value indicated by Arthur et al. (1992d) was confirmed by the producer of the fiber, the K values were then calculated with eq 1 using the extracted amounts of each compound in the seven cases for which the equilibrium could be characterized and the effect of ethanol quantified. The observed values for K_0, K_5, K_{10}, and K_{15}, corresponding to the solutions containing 0, 5, 10, and 15% of ethanol, respectively, are listed in Table 3.

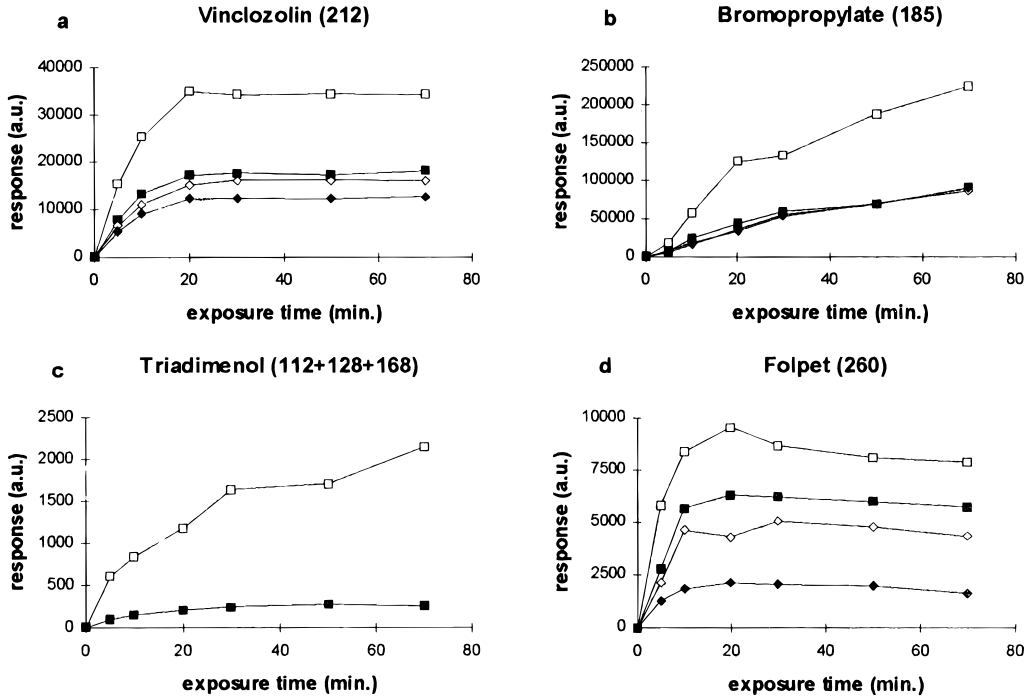

Figure 2. Effect of the ethanolic concentration of the aqueous solution [(□) 0%, (■) 5%, (◇) 10%, (◆) 15%] on the peak area (specific ions) of the four analytes selected as models and extracted by SPME to exposure time: vinclozolin (model a), bromopropylate (model b), triadimenol (model c), and folpet (model d).

Table 3. Variation of Partition Coefficients According to the Ethanolic Concentration of the Aqueous Solution at Equilibrium

		K_5[b]		K_{10}[c]		K_{15}[d]	
compound	K_0[a]	obs	model	obs	model	obs	model
DPA	96	54	68	45	49	35	34
lindane	108	65	77	55	55	42	38
parathion-methyl	93	59	66	49	47	30	33
vinclozolin	97	51	69	45	49	35	35
dichlofluanid	175	82	124	65	89	57	62
procymidone	39	20	28	17	20	13	14
phosalone	630	215	446	199	320	138	224

[a] Pure water solution. [b] 5% ethanolic solution. [c] 10% ethanolic solution. [d] 15% ethanolic solution.

The variation of K versus the polarity parameter of the liquid phase for a given compound has also been mathematically modeled (Snyder, 1974, 1978), and the model has been tested by Arthur et al. (1992c) for methanolic aqueous solutions. Thus K_x, the partition coefficient of a compound in the aqueous solution containing x% of ethanol, can be deduced from K_0 by the relationship

$$K_x/K_0 = 10^{(P_x - P_0)/2} \quad (2)$$

where P_x and P_0 are the solvent polarity parameters for the aqueous solution containing x% of ethanol and water, respectively. The polarity parameter P_x is calculated from P_{EtOH} and P_{H_2O} in the expression

$$P_x = \phi_{EtOH} P_{EtOH} + \phi_{H_2O} P_{H_2O} \quad (3)$$

where ϕ_{EtOH} and ϕ_{H_2O} are the fractions of ethanol and water in the liquid phase, respectively.

The two calculated values, K_x observed and K_x modeled, seem to match at the different ethanolic concentrations for DPA, lindane, parathion-methyl, vinclozolin, and procymidone. The latter two compounds belong to the same chemical class, but no useful correlation can be made. For the other compounds, the polarity parameter of the solution does not appear as the dominant factor for the variation of the distribution constant, even at the concentration of 15% ethanol, which corresponds to the maximum alcoholic concentration in wines.

Comparison between Wines and Alcoholic Solutions. To correlate these observations concerning extraction of pesticides from ethanolic aqueous solutions by SPME with those obtained by the same method in natural matrixes, such as wines, analysis of two commonly commercialized European wines (a red and a white) were performed in triplicate on samples poured out of freshly opened bottles and diluted as indicated to reduce their alcoholic concentration to the level of 10% (wines A). No traces of the selected pesticides were detectable in either wine extract with the ion trap mass detector by this method.

New samples of the same wines were spiked (wines B) at the level of 20 ppb (w/v) with the 10 compounds that were found to be easily detectable in the previous experiments (all except metalaxyl, triadimenol, and folpet). Then, 3-mL aliquots were extracted in triplicate by SPME and chromatographed as described in the usual procedure. Results were compared with those obtained from a 10% alcoholic aqueous solution of the same products, and the ratios of averaged peak areas to corresponding peak areas from a pure water solution were calculated for each compound. These ratios are indicated in Table 4, and the RSDs obtained for peak areas for the three types of samples are listed in Table 5.

The results in Table 4 show that the influence of ethanol on the efficiency of the SPME method to extract these residues in water or in natural wines seems to be of the same order. The concentration of 10% ethanol is the main parameter inducing variations of the partition coefficients between the adsorbing phase and the liquid for each studied compound. The results in Table 5 reveal that the behavior of some of the compounds (i.e., DPA, flusilazole, phosalone) toward this extraction

Table 4. Reduction Indices[a] for Peak Areas in SPME Extractions of Matrixes Containing 10% Ethanol Compared with Pure Water

matrix	DPA	lindane	parathion-methyl	vinclozolin	dichlofluanid	procymidone	dieldrin	flusilazole	bromopropylate	phosalone
10% ethanolic water	0.44	0.50	0.53	0.50	0.38	0.43	0.37	0.12	0.32	0.28
red wine	0.45	0.43	0.43	0.43	0.32	0.37	0.28	0.06	0.30	0.17
white wine	0.34	0.48	0.72	0.50	0.39	0.41	0.26	0.20	0.30	0.32

[a] Ratios of average values in triplicate SPME extractions for 30 min from 20-ppb spiked solutions with a 100-μm PDMS coated fiber.

Table 5. Relative Standard Deviations[a] Relative to Peak Areas in Extracting Matrixes Containing 10% Ethanol Determined by SPME

matrix	DPA	lindane	parathion-methyl	vinclozolin	dichlofluanid	procymidone	dieldrin	flusilazole	bromopropylate	phosalone
10% ethanolic water	3.66	4.05	4.63	9.6	5.1	1.05	9.38	7.54	11.81	12.3
red wine (B)	1.08	1.03	11.33	1	7.16	6.09	44.47	61.07	25.70	39.08
white wine (B)	23.23	4.53	1.37	2.13	2.25	17.27	21.83	13.21	13.5	4.69

[a] SPME extractions in triplicate for 30 min from 20-ppb spiked solutions with a 100-μm PDMS fiber.

method is not the same in 10% ethanolic water, in a red wine, or in a white one. The important decrease of the extraction reproducibility in both wines compared to that in water indicates that other wine constituants interfere with the extraction (sugars, tartrates, phenols, etc.).

CONCLUSION

The accuracy of the SPME method combined with GC-MS for the determination of pesticide residues has been exemplified once more. In addition, new classes of pesticides, technically usable for vineyard protection, are easily detected by this method in aqueous solutions. The presence of ethanol in the extracted solution is an important parameter for the extraction method efficiency. When the partition equilibrium between the solid and the liquid phases was obtained, variation of the ethanolic concentration from 0 to 15% induced no change in the time necessary to reach this equilibrium. In contrast, the extracted amounts of pesticides were deeply affected according to the nature of the product and the alcoholic content of the solution. For some compounds (DPA, lindane, parathion-methyl, vinclozolin, and procymidone), equilibrium constants vary according to the model proposed by Snyder by ethanolic concentration and are based on the polarity parameters of the solution. Compared with observed K_0 values for pure water solutions, observed and modeled K_x values for 5, 10, and 15% ethanol solutions decrease in the same proportion. The PDMS-coated fiber used is not suitable for analysis of compounds like metalaxyl or triadimenol for which the accumulation effect was found to be too small. Moreover, it is clear that folpet, which is suspected to have a role in the fermentation process of grape juices, has to be followed through its degradation products in such a study.

These results indicate that SPME is potentially a powerful tool for the efficient investigation of pesticide residues in wines, but other parameters have to be carefully accounted for because wines are natural matrixes and are much more complex than water.

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