

A Study of the Behavior of Polar and Nonpolar Solid-Phase Microextraction Fibers for the Extraction of Maillard Reaction Products

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Abstract

Aqueous solutions of Maillard reaction products are analyzed using nonpolar and relatively polar solid-phase microextraction (SPME) fibers. The behavior of the polydimethylsiloxane (nonpolar) and carbowaxdivinylbenzene (CWDVB, polar) fibers toward these solutions over a concentration range of 0.005–50 ppm is described. Both fibers demonstrate a marked tendency to selectively adsorb the more highly alkyl-substituted components relative to their comparable proton-substituted counterparts. The CWDVB fiber is found to be more selective for the more polar Maillard reaction products. By employing SPME, gas chromatography, selected ion monitoring (SIM), mass selective detection, and a relatively short exposure time of 10 min, a detection limit in the range of unit parts per billion is established for the fibers. The addition of NaCl to the aqueous solutions significantly increases the amounts of adsorbed components. A linear response between average analyte SIM area counts and analyte concentration over the range of 0.005–0.50 ppm is demonstrated for many of the components.

Introduction

The solid-phase microextraction (SPME) approach has been shown to be a relatively inexpensive, solvent-free, rapid, effective method for the extraction of organic compounds (1–12). Examples include BTEX (benzene, toluene, ethylbenzene, and xylenes), phenols, butter flavors, coffee, juices, explosives, tobacco smoke, and essential oils. Not only have aqueous samples been examined, but experiments that employed the fibers as a tool for the examination of the headspace above the solutions have been described (6,10,11,13). These research results have clearly documented that several factors are critical for the successful use of the SPME fiber for qualitative and quantitative analyses. Among these are fiber type polarity, liquid and headspace volumes, agitation, ionic strength, temperature, fiber exposure time, analyte characteristics, and analyte concentration.

Previous work in our laboratory has shown that an SPME fiber coated with a 100- μm -thick film of polydimethylsiloxane (PDMS) was very effective in the qualitative analysis of volatile

and semivolatile Maillard reaction products (10). The structure of the model compounds was shown to have a very dramatic effect on the rate, equilibrium time, and amount of compound adsorbed onto the fiber. The presence of multiple components in an aqueous solution at approximately 50 $\mu\text{g}/\text{mL}$ resulted in a significant competition for adsorption onto the fiber. Also, increases in the amount and rate of adsorption were found when NaCl was added to the aqueous solutions. This report describes how additional factors (as well as those previously observed) affect the qualitative and quantitative aspects of employing polar and nonpolar SPME fibers for the analysis of aqueous solutions of volatile and semivolatile Maillard reaction products.

Experimental

Standard solutions

All organic compounds were obtained from Aldrich Chemical (Milwaukee, WI) and used as received. Standard aqueous solutions were prepared gravimetrically at approximately 50 ppm ($\text{ng}/\mu\text{L}$) using deionized water. Analysis of a blank water sample revealed no chromatographic interferences. Calibration curves were generated from serial dilutions of a stock solution of each component or mixture of components. Reagent-grade NaCl and NaClO_4 were used to prepare the "salt"-containing solutions.

Methylene chloride from Burdick and Jackson Laboratories (Muskegon, MI) was used to prepare organic solutions of known concentrations. These solutions were used to obtain response factors for known amounts of each analyte.

Instrumental conditions

A Hewlett-Packard (Wilmington, DE) 5880 gas chromatograph (GC) was fitted with a Hewlett-Packard 5970 mass selective detector (MSD) operating at 70 V in the electron impact mode and a flame-ionization detector (FID). The split ratio for the MSD–FID was approximately 80:20. The MSD was used for structure confirmation, whereas FID area counts were used for quantitative purposes. The MSD interface temperature was

225°C, and the GC injection port was set at 250°C. The GC was furnished with a DB-1701 fused-silica column (30 m × 0.32-mm i.d., 1.0- μ m film thickness) (J&W Scientific, Folsom, CA). The column linear velocity was set at approximately 40 mL/min. The GC oven was temperature-programmed from 10 to 220°C at 20°C/min. Splitless injections were used, and the split valve was opened after 2 min.

A second GC-MSD system consisting of an HP 5890 series II Plus GC equipped with an HP 5972 MSD was used to gain an appreciation of the lower detection limits for SPME extraction of very low analyte concentrations. The GC was fitted with a DB-WAX fused-silica column (30 m × 0.25-mm i.d., 0.5- μ m film thickness) (J&W Scientific). The MSD interface and GC injection port temperatures were 250°C. The GC oven was temper-

ature-programmed from 40 to 240°C at 5°C/min. Splitless injections of the SPME fibers were made, and the split was opened 1 min after injection. The MSD was operated in the selected ion monitoring (SIM) mode.

General SPME procedures

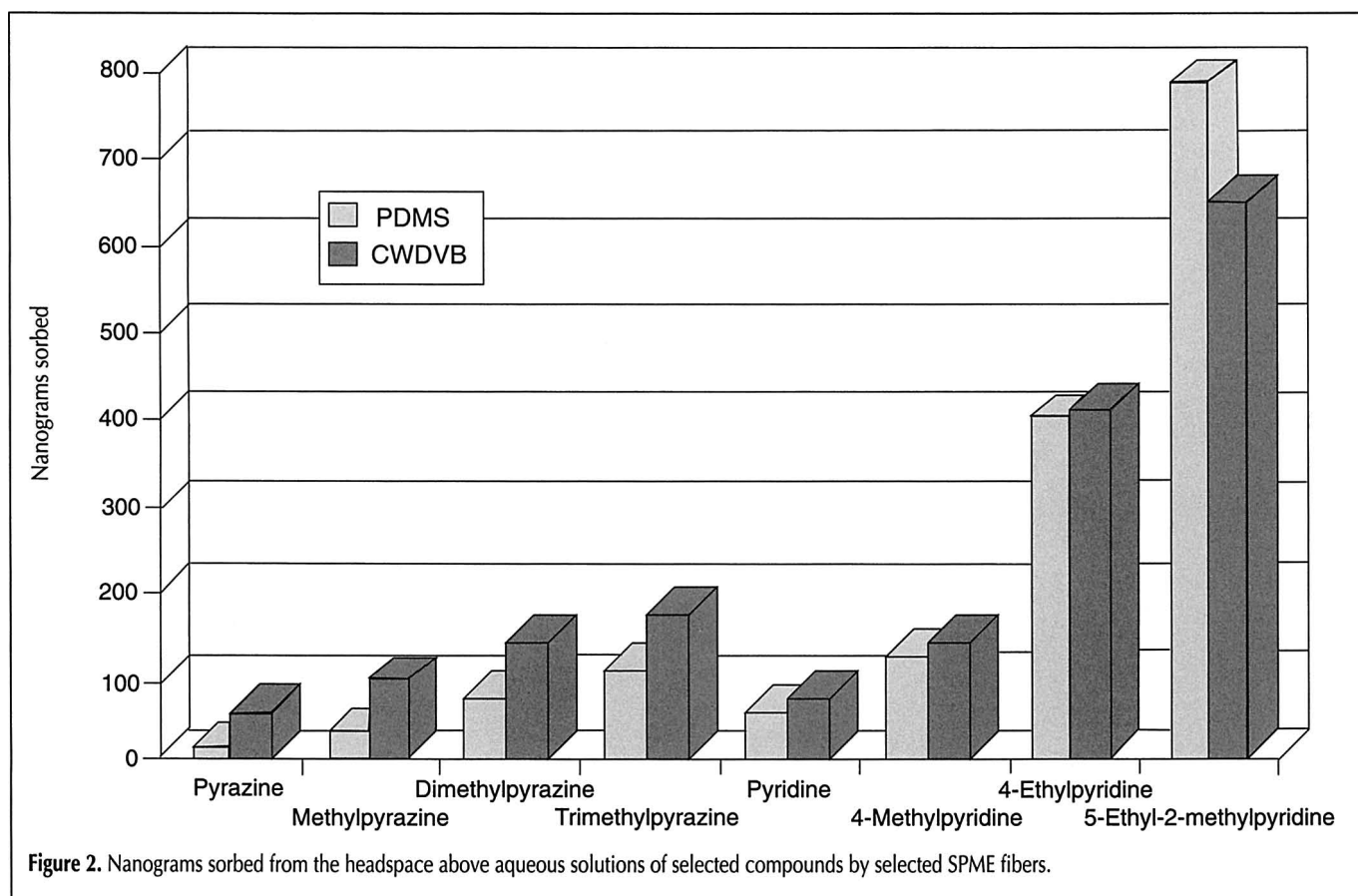
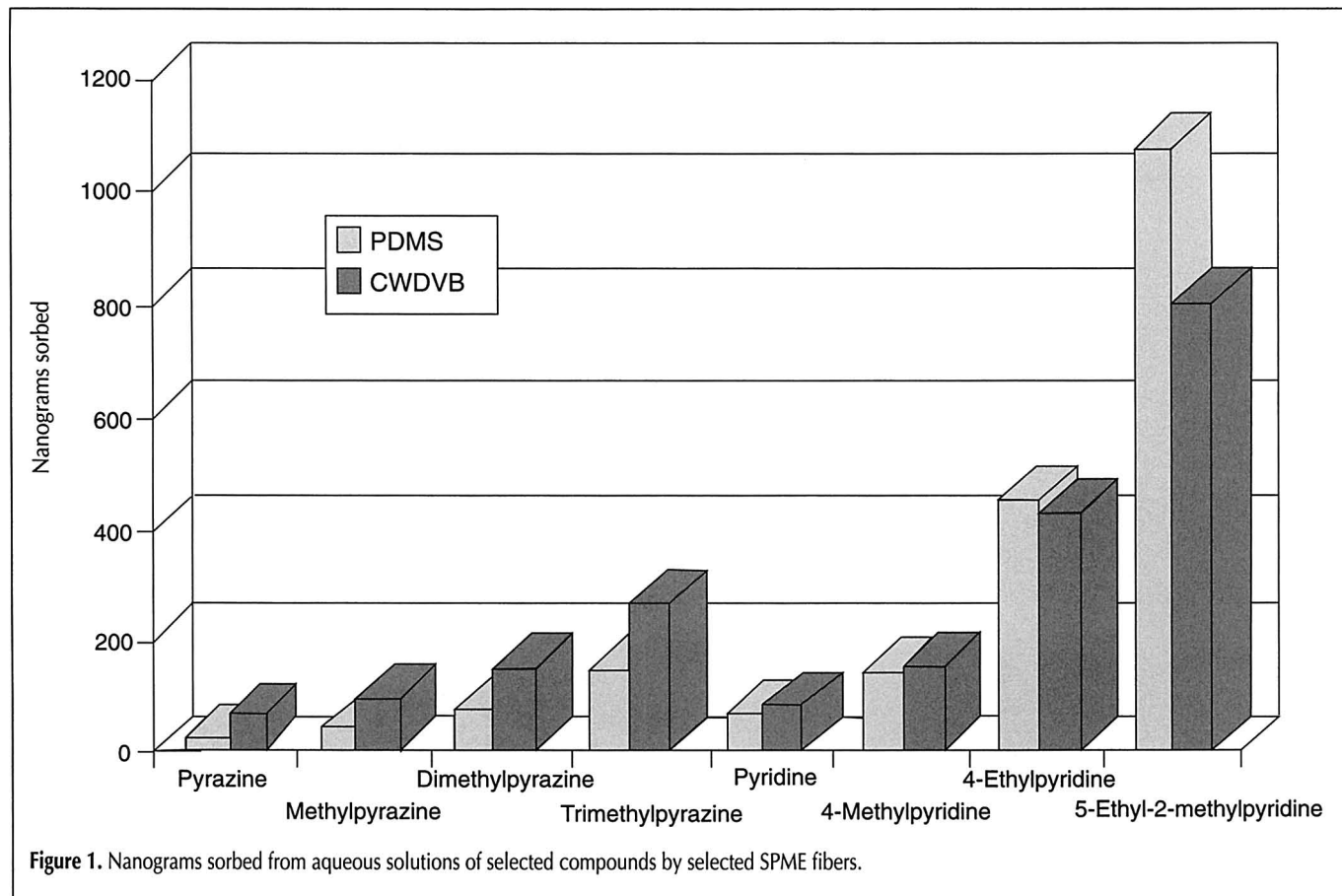
For thermal desorption of the exposed SPME fiber, the manual injection method was followed as described by the manufacturer (Supelco, Bellefonte, PA). The thermal desorption time in the injection port at 250°C was held constant at 10 min. No carryover was observed using this approach. Thus, a freshly conditioned fiber was available for re-exposure. Two types of fibers were used: polydimethylsiloxane (PDMS) (100 μ m, part #5-7300) and carbowaxdivinylbenzene (CWDVB) (65 μ m, part

Table I. Nanograms Sorbed for Selected Compounds as a Function of Concentration and SPME Fiber Type

Concentration (ppm)	Thiazole*	Thiazole [†]	Methylthiazole*	Methylthiazole [†]	Dimethylthiazole*	Dimethylthiazole [†]
50	16.11	46.45	60.01	125.02	175.42	258.99
5	1.52	7.08	7.63	28.26	23.19	66.54
0.5	0.13	0.75	0.71	4.57	2.14	11.41
	Trimethylthiazole*	Trimethylthiazole [†]	Ethoxythiazole*	Ethoxythiazole [†]		
50	513.51	490.28	259.24	606.87		
5	82.68	127.02	28.05	144.32		
0.5	8.12	20.93	1.70	19.16		
	Pyridine*	Pyridine [†]	4-Methylpyridine*	4-Methylpyridine [†]	Pyridine alone*	Pyridine alone [†]
50	64.08	81.69	141.29	152.16	74.75	152.70
5	9.78	11.41	22.65	29.55	9.11	24.07
0.5	0.92	2.28	2.74	7.18	not detected	1.67
	4-Ethylpyridine*	4-Ethylpyridine [†]	5-Ethyl-2-methylpyridine*	5-Ethyl-2-methylpyridine [†]		
50	452.75	426.77	1,072.70	800.83		
5	72.03	96.66	163.76	184.70		
0.5	7.30	19.07	16.00	25.57		
	Pyrazine*	Pyrazine [†]	Methylpyrazine*	Methylpyrazine [†]		
50	24.93	61.21	37.39	96.17		
5	2.89	7.56	4.48	17.66		
0.5	not detected	1.44	0.41	2.37		
	2,3-Dimethylpyrazine*	2,3-Dimethylpyrazine [†]	Trimethylpyrazine*	Trimethylpyrazine [†]		
50	75.29	149.03	146.33	262.46		
5	10.20	32.95	19.89	59.80		
0.5	0.11	5.12	0.23	8.95		
	2-Methoxypyrazine*	2-Methoxypyrazine [†]	2-Methoxy-3-methylpyrazine*	2-Methoxy-3-methylpyrazine [†]	Acetylpyrazine*	Acetylpyrazine [†]
50	135.90	424.54	282.22	574.23	28.15	129.81
5	17.35	114.51	36.51	146.55	2.30	24.88
0.5	2.07	19.87	3.57	22.65	not detected	3.12
	Furfural*	Furfural [†]	5-Methylfurfural*	5-Methylfurfural [†]		
50	36.57	285.15	83.45	729.15		
5	2.02	50.77	7.17	135.92		
0.5	not detected	6.73	not detected	17.23		

* Polydimethylsiloxane fiber

[†] Carbowaxdivinylbenzene fiber



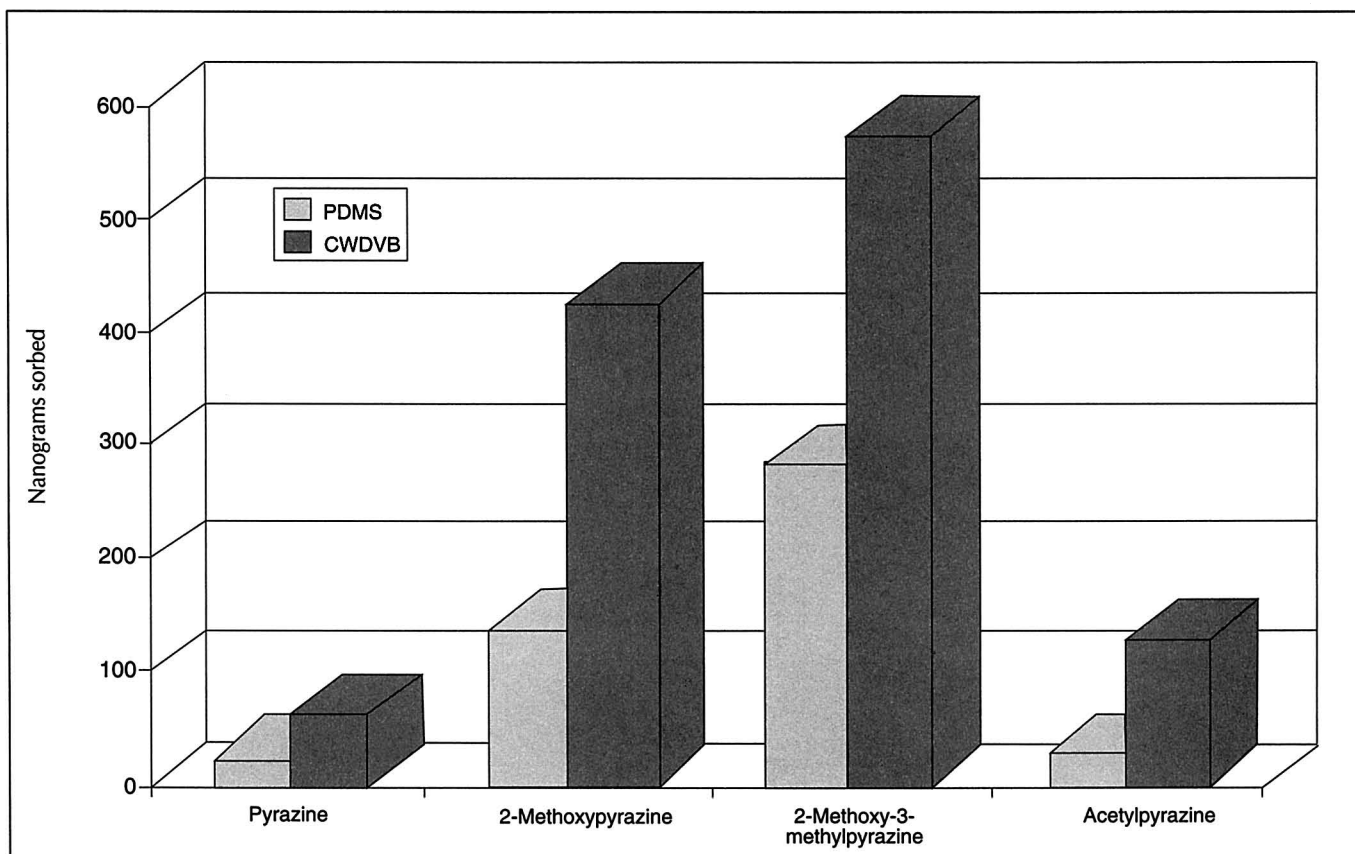


Figure 3. Nanograms sorbed from aqueous solutions of selected compounds by selected SPME fibers.

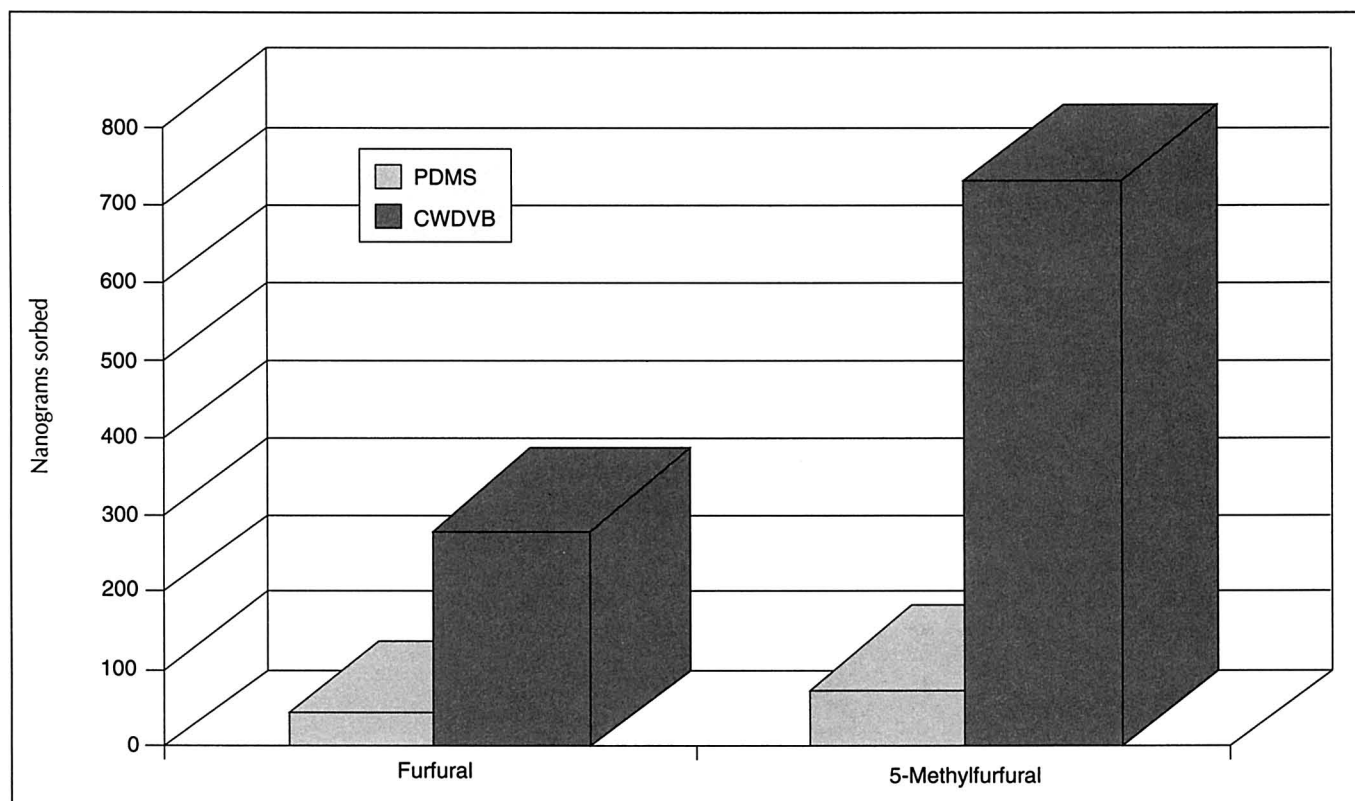


Figure 4. Nanograms sorbed from an aqueous solution of furfurals by selected SPME fibers.

#5-7312). For both liquid and headspace sampling, 10 mL of the aqueous solution containing the analyte(s) of interest at the selected concentration was placed in a 20-mL vial along with a small 7- × 2-mm magnetic stirring bar. The vial was immediately capped upon addition of the solution. The dimensions of the sealed vial were approximately 2 cm in diameter and 6.5 cm in height. Once the aqueous solution was placed in the sealed vial, it was allowed to stand undisturbed overnight before sampling. When both the liquid and headspace sampling occurred, the solution was stirred at such a rate that the vortex was approximately 1 cm deep. For liquid sampling, the entire fiber was immersed to a constant depth for 10 min. For headspace sampling, the fiber was suspended at a constant height of 0.5 cm above the stirring solution for 10 min. Fresh samples were used for each measurement, and five measurements were used for each determination. An average relative standard deviation (RSD) of 5% was found for all determinations, which coincided with previous findings (10) on similar compounds.

Results and Discussion

Using two SPME fibers of differing polarities, responses versus concentration for 20 aroma and flavor compounds associated with the Maillard reaction and sugar thermal degradation were

generated. By using a 100- μ m-thick PDMS fiber and a 65- μ m-thick CWDVB fiber, responses over the range of approximately 0.005–50 ppm for selected volatile aldehydes, pyrazines, pyridines, and thiazoles were collected with an FID and an MSD operating in the SIM mode. By using a splitter on the outlet of one of the DB-1701 GC columns, the identities of the eluted components were simultaneously confirmed with MSD.

Previous examinations (10) of the behavior of these compound classes toward SPME analyses have shown that an exposure time of 10 min for a 100- μ m-thick PDMS fiber in a stirred aqueous solution was sufficient to establish a consistent amount of adsorbed material at concentrations less than or equal to 50 ppm. Therefore, for all of the values quoted in this study, a fixed exposure time of 10 min was adopted. The number of nanograms adsorbed was calculated from response factors obtained through splitless injections of known concentrations of the analytes dissolved in methylene chloride. The values listed in Table I were determined from aqueous solutions containing multiple compounds of a specific class. For example, the values for the thiazoles were obtained from an aqueous solution containing all the thiazole derivatives. In one case, however, the behavior of the fibers toward an aqueous solution containing only pyridine was investigated. Five replicates of each extraction were performed, and on average, the RSD for the five injections was less than $\pm 5\%$.

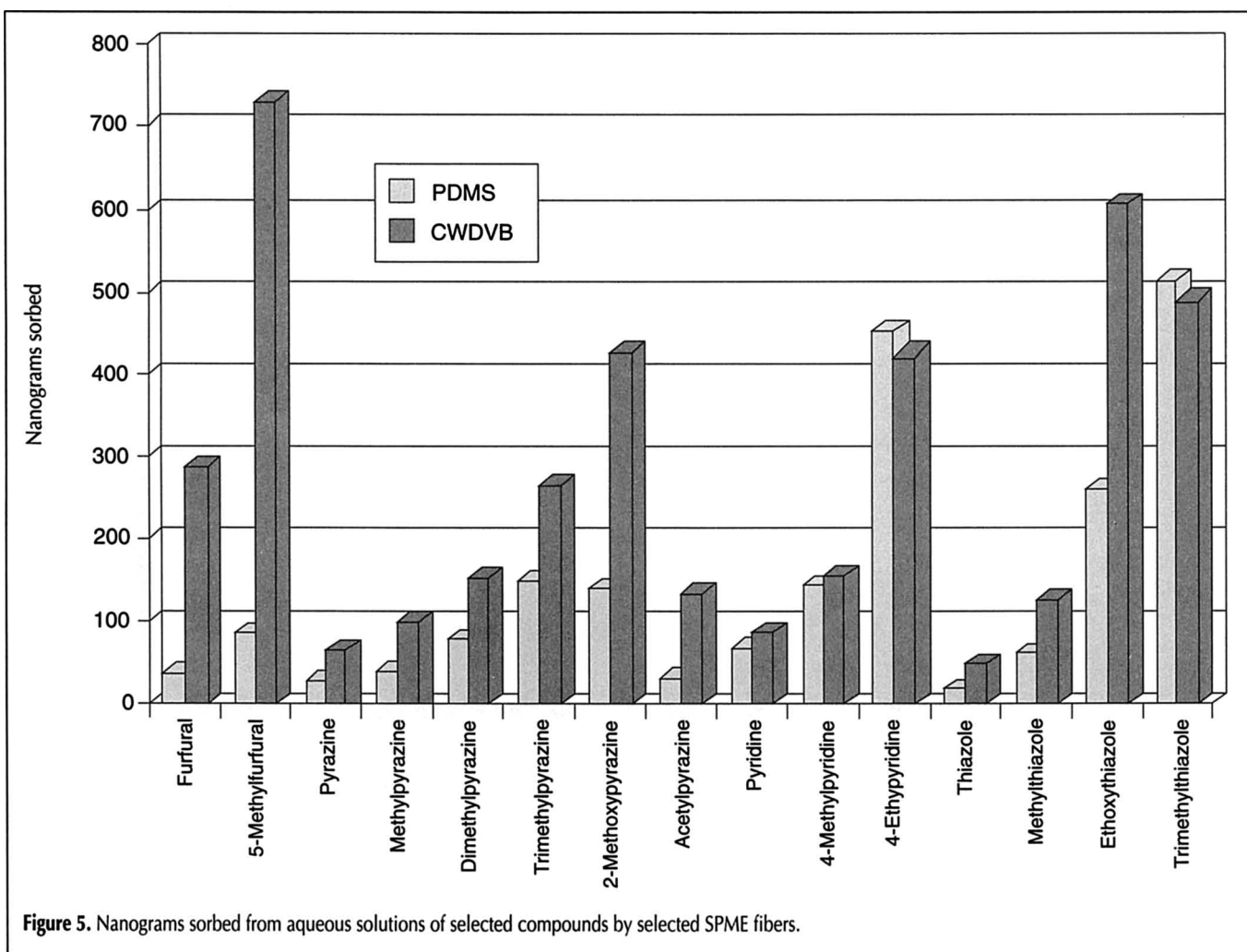


Figure 5. Nanograms sorbed from aqueous solutions of selected compounds by selected SPME fibers.

Fiber selectivities

The two fibers displayed some rather dramatic selectivities from a variety of perspectives (Table I). The amount of compound adsorbed by both the nonpolar PDMS and relatively polar CWDVB fibers increased with the degree of alkyl substitution, even though all the compounds were at the same concentration.

In an aqueous solution containing approximately 50 ppm of pyrazine, methylpyrazine, dimethylpyrazine, and trimethylpyrazine, both the PDMS and CWDVB fibers adsorbed approximately four times more trimethylpyrazine than pyrazine. Specifically, the PDMS fiber adsorbed 24.93 ng of pyrazine and 146.33 ng of trimethylpyrazine from an aqueous solution containing

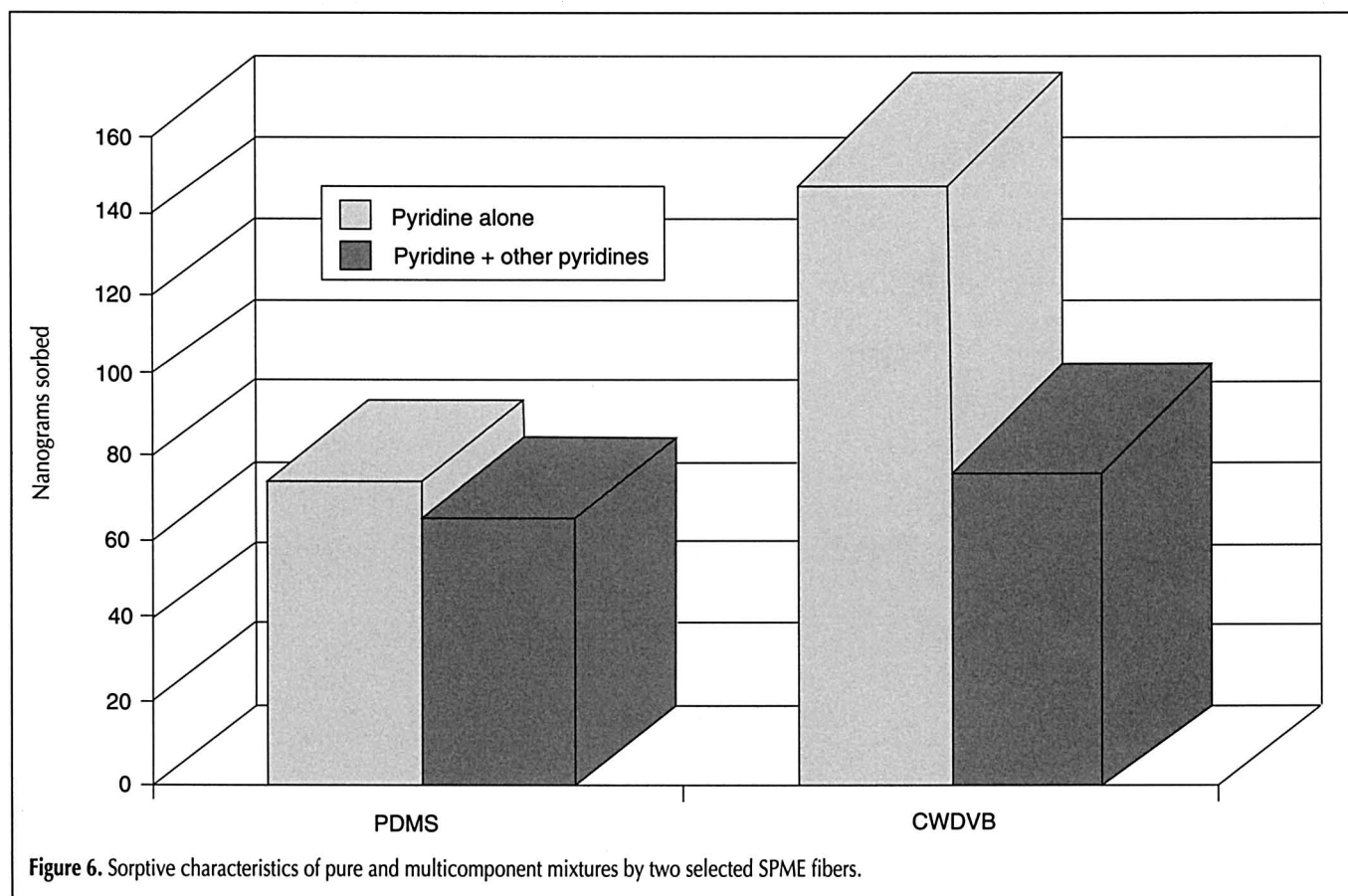
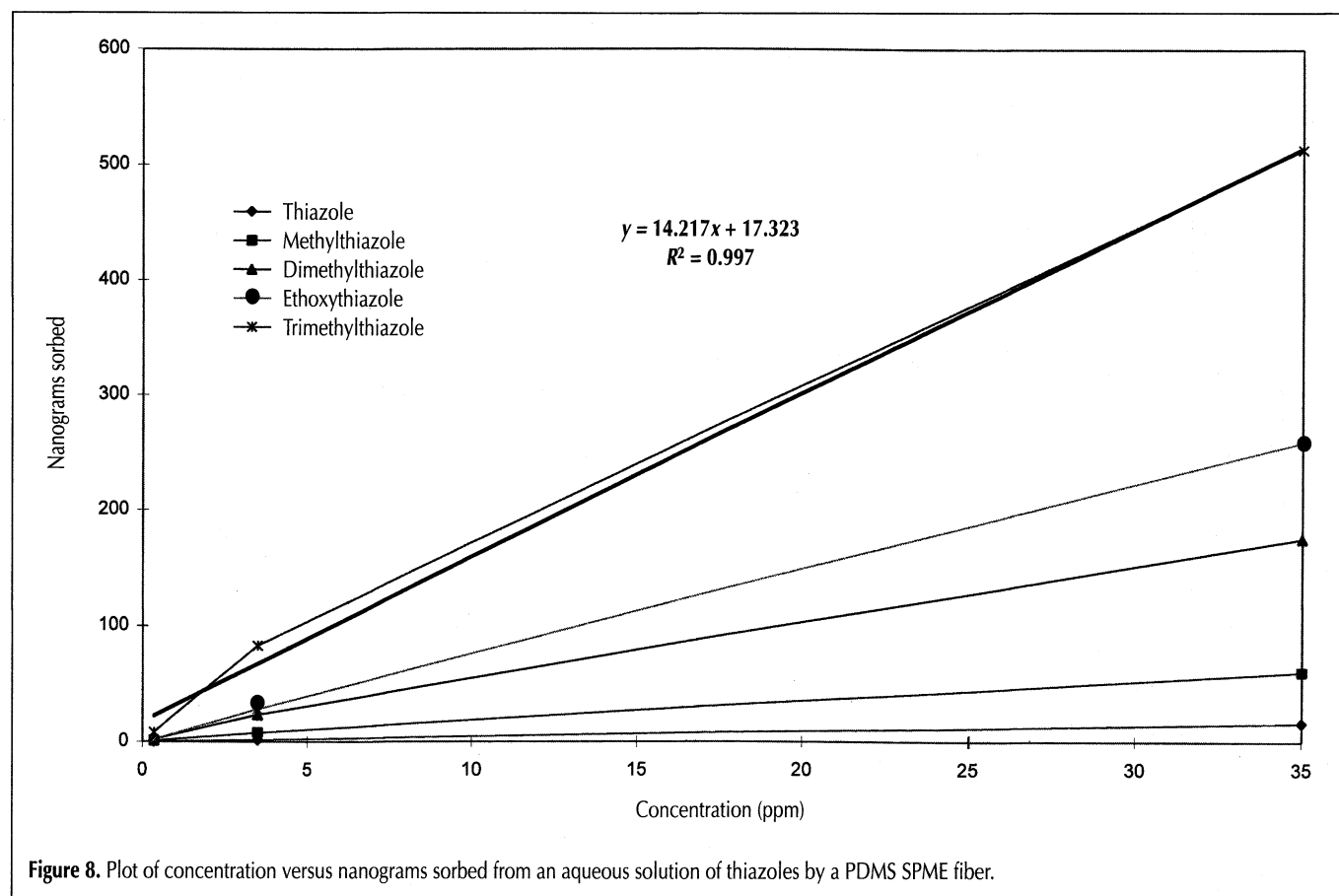
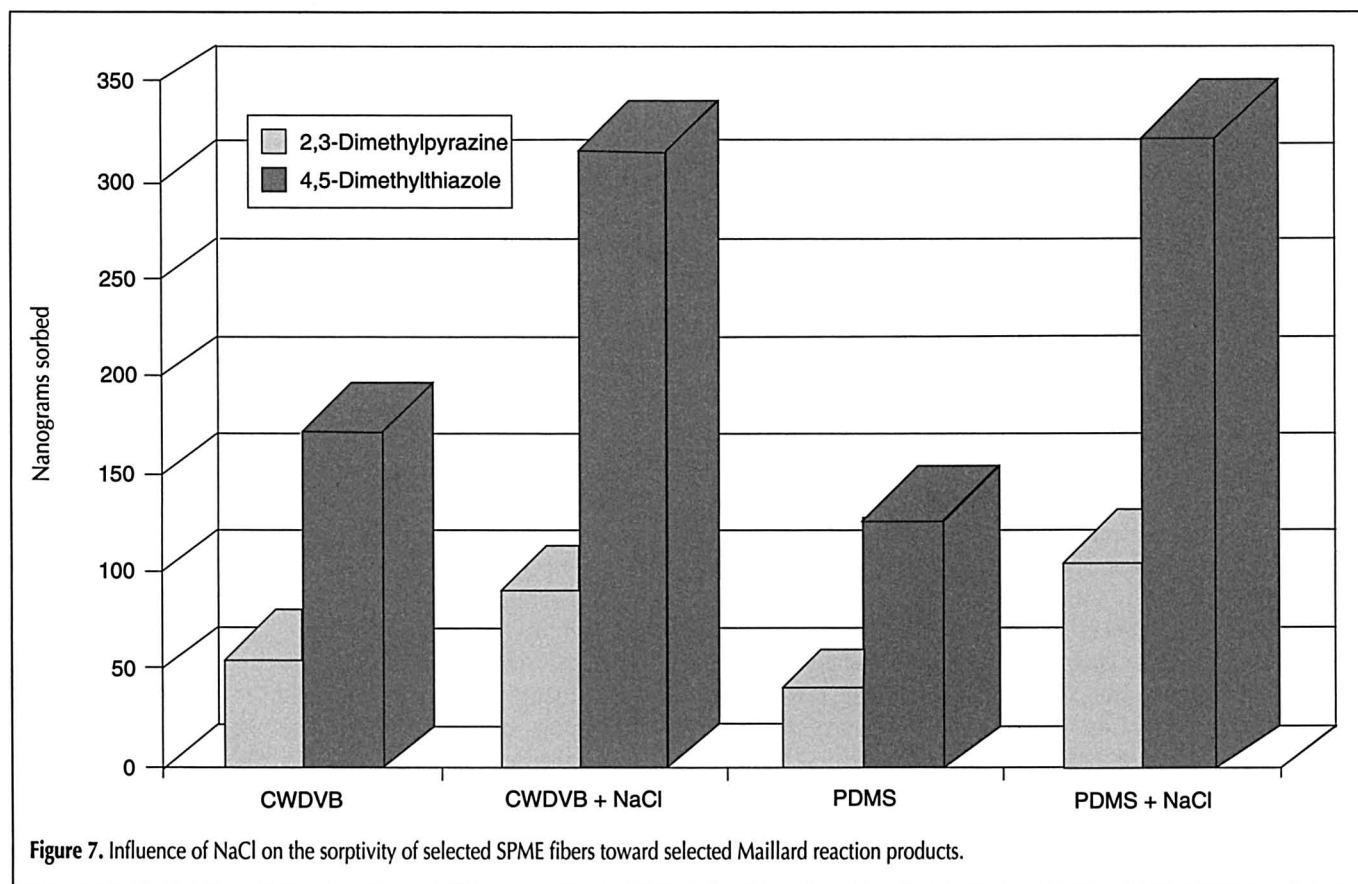


Figure 6. Sorptive characteristics of pure and multicomponent mixtures by two selected SPME fibers.

Table II. Behavior of Selected SPME Fibers Toward Solutions of Maillard Reaction Products

	20-Component mix adsorption (ng)		5-Component mix adsorption (ng)		20-Component mix* adsorption (ng)		20-Component mix† adsorption (ng)	
	CWDVB	PDMS	CWDVB	PDMS	CWDVB	PDMS	CWDVB	PDMS
Pyrazine	29.60	13.23	61.21	24.93	1.56	20.98	not detected	21.86
Thiazole	36.55	19.29	46.44	16.11	63.34	9.81	65.74	45.73
Pyridine	59.13	44.32	81.68	64.07	85.63	12.99	84.05	80.24
4-Methylthiazole	82.58	43.74	125.01	60.01	109.51	51.21	130.02	98.48
Methylpyrazine	36.87	25.19	96.18	37.39	47.09	29.96	55.40	45.44
2,3-Dimethylpyrazine	55.60	39.83	149.04	75.29	63.29	41.96	90.00	104.37
4,5-Dimethylthiazole	172.24	129.31	258.97	175.40	224.76	141.27	316.31	326.35
4-Ethylpyridine	232.85	255.15	426.76	452.74	312.51	260.26	448.38	601.93
2,4,5-Trimethylthiazole	359.72	429.83	490.23	513.46	508.92	518.25	842.23	1,305.11
2,3,5-Trimethylpyrazine	97.05	79.40	262.48	146.34	110.43	82.28	196.25	212.24
5-Methylfurfural	278.43	59.81	729.20	83.46	281.31	60.28	368.54	140.51
5-Ethyl-2-methylpyridine	362.43	493.48	800.73	1,072.58	477.38	531.88	859.84	1,500.76
2-Acetylpyrazine	74.62	26.91	129.81	28.15	52.93	26.74	82.04	41.65

* 0.2 g/mL NaClO₄
† 0.2 g/mL NaCl



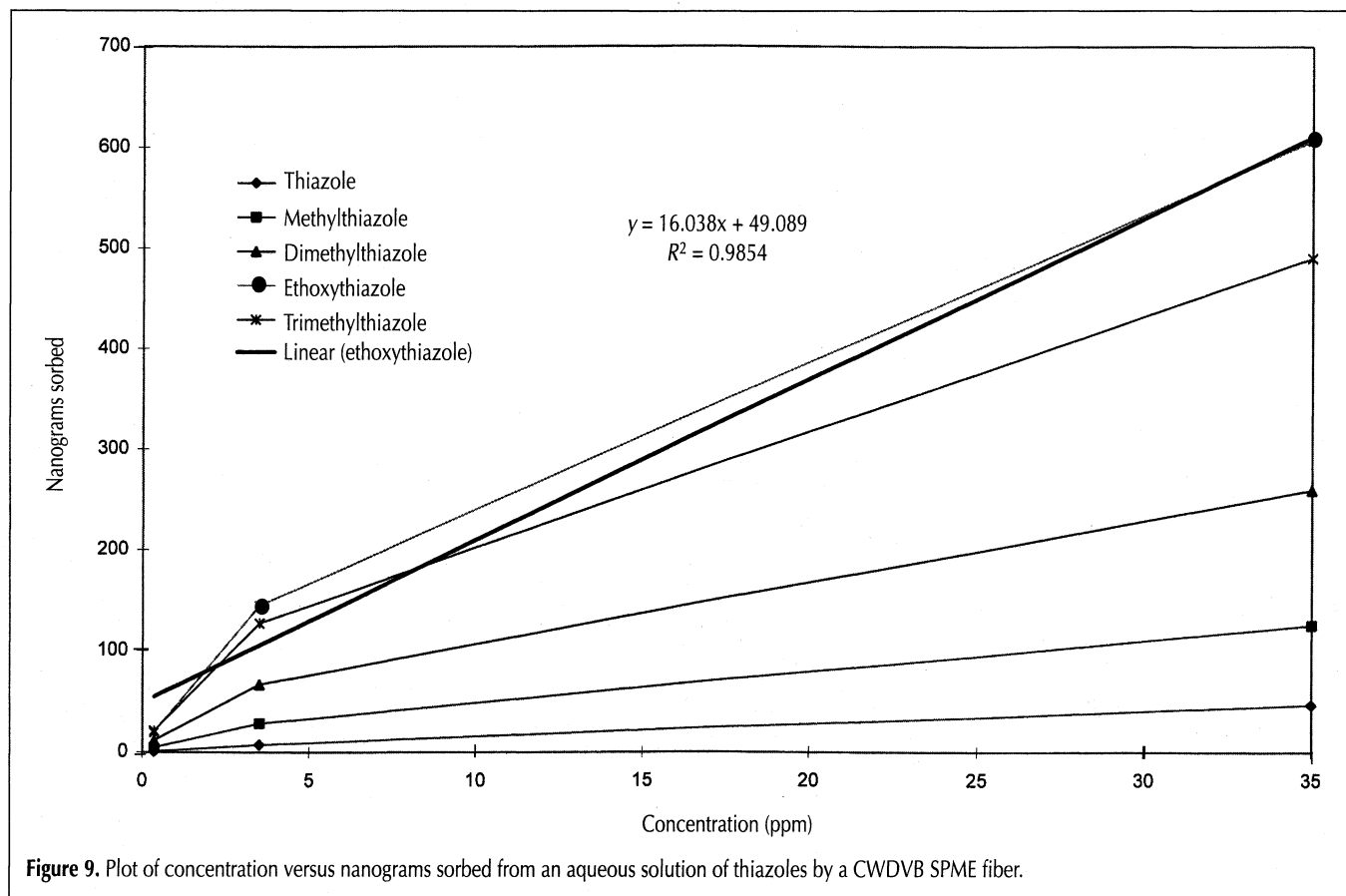
approximately 50 ppm each of substituted pyrazines. In the comparable CWDVB experiment, this fiber adsorbed 61.21 ng of pyrazine and 262.46 ng of trimethylpyrazine. Similar behaviors associated with alkyl substitution were encountered for most of the other alkyl-substituted heterocyclic compounds (Figure 1), relative to their proton counterparts.

The aroma of a particular flavor–aroma formulation rests with olfactory detection of the compounds that reside in the headspace above the formulation (14). It is well-established that roasted natural products produce a wide array of volatile compounds that are linked directly to sensory cues. Some of the more important volatile compounds from roasted natural products that key these sensory cues are pyrazine, pyridine, thiazole, and furan derivatives. An examination of the headspace above aqueous solutions of representative flavor–aroma compounds via SPME revealed trends in their sorptive capacity much like those found in the aqueous solutions. For example, in the headspace above these aqueous solutions, one of which contained a mixture of pyrazines and the other a mixture of pyridines, both fibers displayed a higher selectivity toward derivatives that contained alkyl substituents. Specifically, the PDMS fiber adsorbed 15.65 ng of pyrazine and 109.09 ng of trimethylpyrazine from the headspace above an aqueous solution that contained approximately 50 ppm each of substituted pyrazines. Figure 2 reveals this behavior as similar to that of other alkyl-substituted nitrogen heterocyclic compounds.

From the results of PDMS and CWDVB SPME fibers' exposure to nitrogen heterocyclic compounds containing relatively polar substituents such as a methoxy group or an acetyl group,

a significant selectivity pattern was observed. For example, a PDMS fiber that was exposed to an aqueous solution containing equal concentrations (each approximately 50 ppm) of pyrazine and 2-methoxypyrazine as well as other pyrazine derivatives adsorbed 24.93 ng of pyrazine and 135.90 ng of 2-methoxypyrazine. In contrast, however, the same PDMS fiber adsorbed only 28.15 ng of acetylpyrazine from the aqueous solution. A very similar trend was discovered for the CWDVB fiber (Figure 3). Figure 3 also provides the first glimpse of a significant difference in the sorptive behaviors of the PDMS and CWDVB fibers toward polar species. Additional examples and expanded discussions are given later.

Thermal degradation of sugars plays a very important role in the flavor and aroma of cooked natural products (14). A significant part of the aroma and taste due to thermal degradation of sugars is captured in the sensory characteristics of furfural and its derivatives. Thus, the behavior of the PDMS and CWDVB SPME fibers toward furfural and 5-methylfurfural was examined. From an aqueous solution containing approximately 50 ppm each of furfural and 5-methylfurfural, both fibers demonstrated significant selectivities as a function of alkyl substituent (Figure 4). Specifically, the CWDVB fiber adsorbed 285.15 ng, whereas the PDMS fiber adsorbed only 36.57 ng of furfural from the 50-ppm aqueous solution of furfural and 5-methylfurfural. It is noteworthy to mention that the thicknesses of these two fibers were not equivalent. The PDMS fiber was 100 μm thick, and the CWDVB fiber was only 65 μm thick. Yet apparently, the sorptive characteristics of the film used in the CWDVB fiber are such that the film is capable of



demonstrating a much superior sorptive characteristic toward furfural relative to the PDMS fiber. To test this conclusion (which was based only on the furfural results) for a possible broader generality, direct comparisons were made for the amount of adsorbed compound for the fibers across many of the compounds studied (Figure 5). In the vast majority of cases, the CWDVB fiber adsorbed more material than the PDMS fiber did. Thus, a broad generalization as to the sorptive characteristics of the CWDVB fiber relative to the PDMS fiber cannot be established based on these results. This is because, in a few of these examples, such as 4-ethylpyridine and trimethylthiazole, the PDMS fiber adsorbed an equivalent amount of material. It does appear clear, however, that the widest disparity in sorptive characteristics between the two fibers occurred, for example, with the more polar compounds such as the furfurals, cetylpyrazine, thiazole, and ethoxythiazole (Figure 5).

Fiber capacity

The capacity of the CWDVB fiber to adsorb increased amounts of the more polar compounds can be seen as a distinct advantage in terms of analyte detection limit capability. At relatively low concentrations in the range of 0.5 ppm and in a number of instances, the CWDVB fiber adsorbed enough material to produce a detectable response on the FID (two times the signal-to-noise ratio). At the same relatively low concentration, the PDMS at times adsorbed insufficient amounts of material to be

detected by the FID. These instances occurred in association with PDMS fiber experiments on 0.5-ppm solutions containing pyridine, pyrazine, acetylpyrazine, furfural, and 5-methylfurfural. This detection limit (approximately 0.5 ppm) for these compounds is only representative of what is obtainable by using an FID detector, a 10-min sampling time, and no sample treatment with reagents such as NaCl. Changing the detector to a mass spectrometer operating in the SIM mode, lengthening the exposure time, and adding NaCl would naturally improve the detection limits. Experiments that expand these concepts appear below. Nonetheless, these results clearly indicate the differences in the sorptive characteristics of these fibers.

It is almost intuitive that competition for adsorption onto the fiber will occur if more than one organic species is contained within the aqueous solution. To test the degree of this influence, aqueous solutions were prepared in which (a) pyridine was the sole organic species in the solution and (b) pyridine was in the presence of equal concentrations of 4-methylpyridine, 4-ethylpyridine, and 5-ethyl-2-methylpyridine. The results (Figure 6) for both fibers indicated a significant difference in the amount of pyridine adsorbed from an aqueous solution containing only pyridine at 50 ppm versus the amount adsorbed if pyridine were in the presence of other pyridines in an aqueous solution at 50 ppm each. This observation is most probably not due to a function of the capacity of either of the fibers because more than a microgram of total material can be found

Table III. Ion Area Counts for SPME Sorbed Maillard Reaction Products

Compound	Ions monitored	Concentration (ppm)						
		0.005	0.0125	0.025	0.05	0.5	5	50
<i>CWDVB</i>								
Pyridine	52	28572	52653	100207	196949			
Pyrazine	80, 53	8639	15442	32839	68064	409053	1434446	2053314
Thiazole	85, 58	23497	42650	88074	170481	1178859	3981389	5354858
Methylpyrazine	94, 67	26461	53779	112702	224038	1519401	5511153	5945162
4-Methylthiazole	99, 71	90238	197274	383239	752399	5780144	21156603	22108600
4-Methylpyridine	93, 92	86235	195202	367520	818341	6037018	31183440	47535670
Methoxypyrazine	110, 109	98835	227141	433114	863376	6560456	28031189	33867399
2,3-Dimethylpyrazine	108, 67	59147	129747	254935	521092	3520472	16618641	23572797
Furfural	96, 95	66516	176020	236848	462690	4127842	14877516	26449928
5-Methylfurfural	110, 109	102393	228807	453889	881516	6664835	35476519	90739028
<i>PDMS</i>								
Pyridine	52		6312	8487	16858	125703	741552	4213816
Pyrazine	80, 53		3158	3943	6112	44531	280991	1747778
Thiazole	85, 58		4456	6584	13283	98866	660110	4534370
Methylpyrazine	94, 67		3921	5237	10488	85908	492926	2948424
4-Methylthiazole	99, 71		10410	16712	36377	296143	2043954	13650674
4-Methylpyridine	93, 92		15084	25005	53751	427940	3234546	17666915
Methoxypyrazine	110, 109		7255	11833	27880	239858	1634532	12620717
2,3-Dimethylpyrazine	108, 67		8150	14082	28641	215981	1296117	7164404
Furfural	96, 95				43808	164447	780109	4968343
5-Methylfurfural	110, 109		12585	29543	42029	213710	1173693	859399

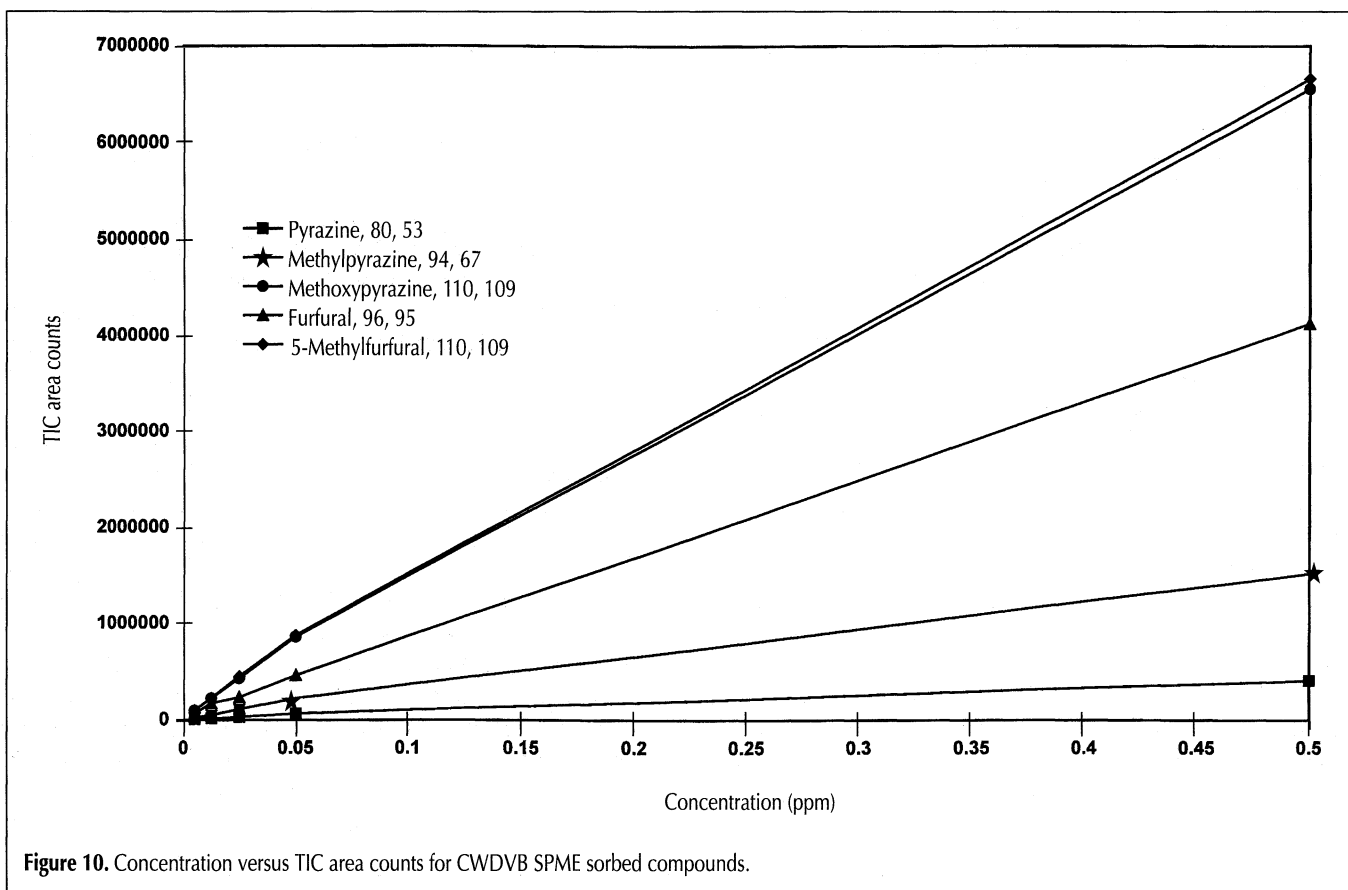


Figure 10. Concentration versus TIC area counts for CWDVB SPME sorbed compounds.

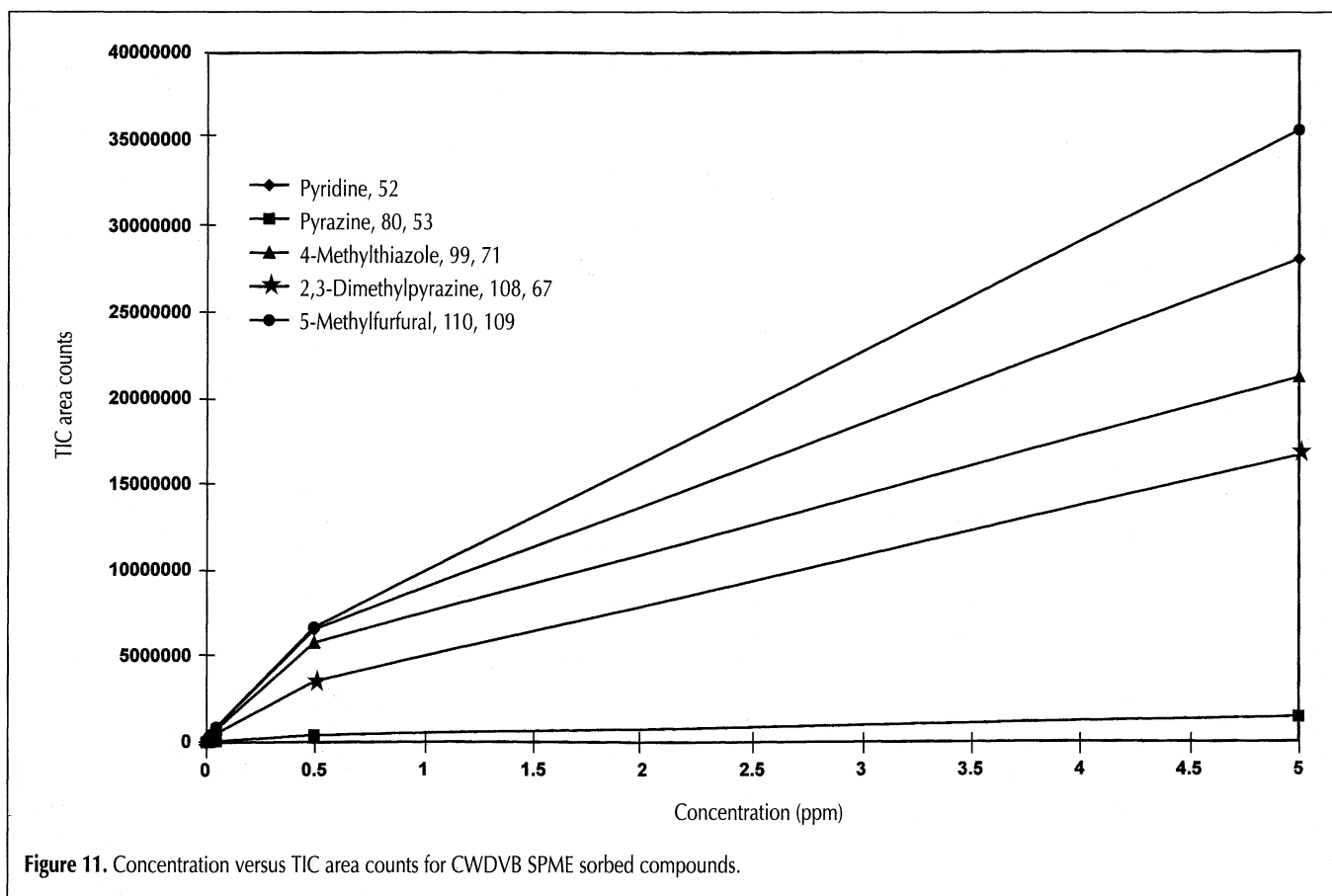


Figure 11. Concentration versus TIC area counts for CWDVB SPME sorbed compounds.

on any one of the fibers after exposure to a 50-ppm multicomponent aqueous solution. Thus, it appears that adsorption of the more nonpolar alkyl substituents could ultimately either retard, displace, exclude, or compete more favorably for adsorption than the more polar compounds can. Certainly it might be expected that the Carbowax component of the CWDVB fiber should preferentially have affinity for more polar substituents. Yet these more nonpolar substituents were preferentially adsorbed. However, as was mentioned earlier, the CWDVB fiber still outperformed the PDMS fiber in sorptivity toward the more polar compounds.

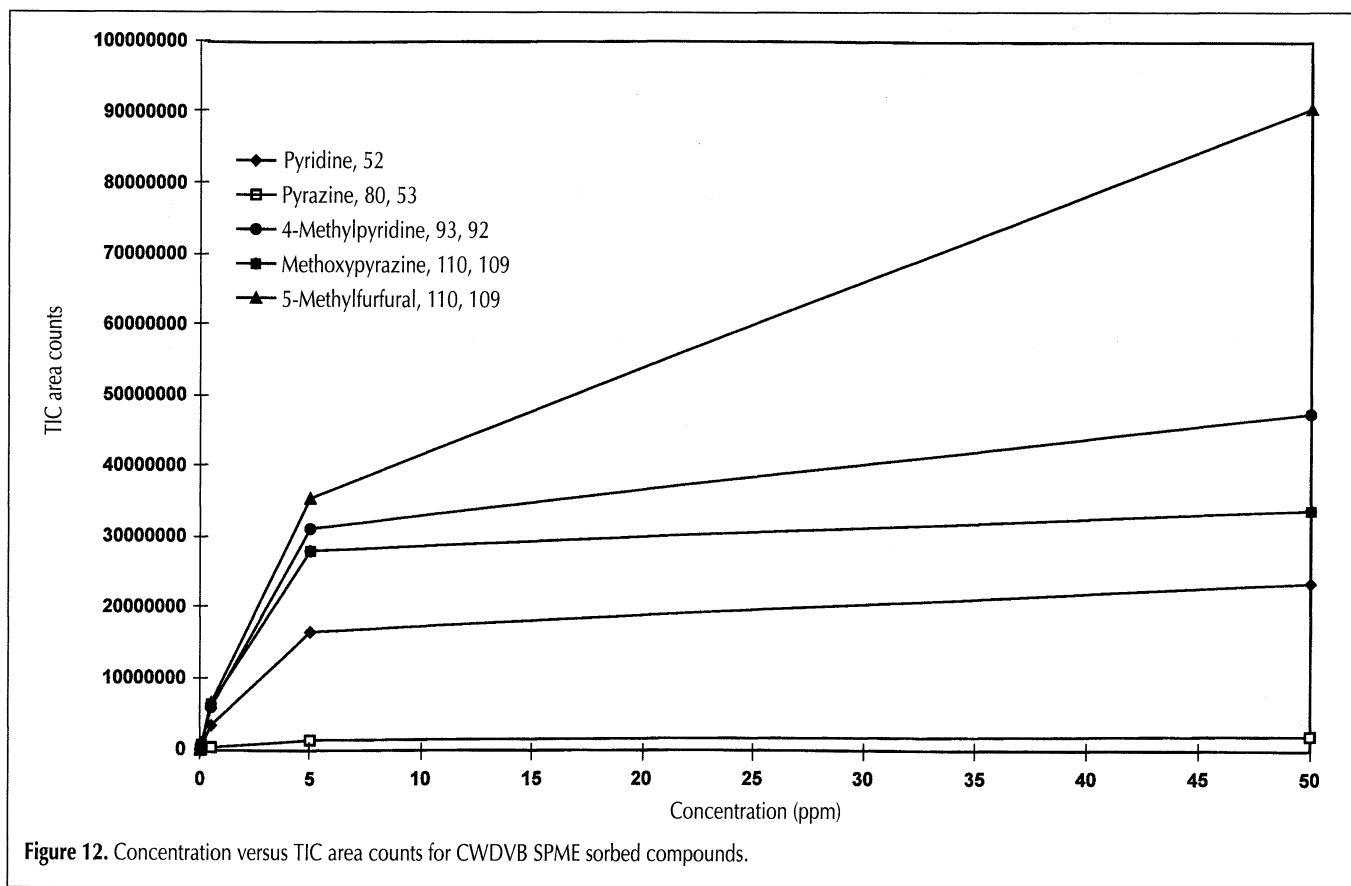
Roasted natural products are known to produce a complex variety of volatile and semivolatile components (14). Thus, to more fully describe this difference in sorptivity displayed by the fibers toward pyridine in pure solution versus in the presence of other pyridines, a relatively complex mixture of 20 Maillard-reaction-type volatile compounds, most of which are described in this report, was examined using the PDMS and CWDVB SPME fibers (Table II). The results, when compared to the simpler less complex mixtures, confirmed that the presence of multiple components alters the resultant net adsorption of the fibers for these compounds. For example, in the 20-component mix containing approximately 50 ppm of each component, the CWDVB fiber adsorbed 82.58 ng of 4-methylthiazole, but in a less complex aqueous solution containing only 4-methylthiazole and four other thiazoles also at 50 ppm, the CWDVB fiber adsorbed 125.01 ng of 4-methylthiazole. In a similar fashion, with the PDMS fiber, 44.32 ng of pyridine was adsorbed from the 20-component mix, whereas 64.07 ng was

adsorbed in a less complex solution containing only pyridine and three other substituted pyridines. This trend was repeated for all of the components.

Influence of ionic strength

The addition of salt to aqueous solutions that contain dissolved organic species has been shown to dramatically improve the adsorption characteristics of SPME fibers. For example, the addition of salt (NaCl) to aqueous solutions of pesticides (8), fatty acids (15), and Maillard reaction products (10) resulted in increased sorptivity of the SPME fibers, which in turn resulted in lower detection limits. Table II contains data indicating that similar results were obtained with CWDVB and PDMS fibers when the ionic strength of the aqueous solution was increased using NaClO_4 and NaCl at 0.2-g/mL concentrations. Addition of NaClO_4 to the 20-component mixture followed by analysis with the CWDVB fiber revealed that significant increased amounts of material had been adsorbed for all components with the exception of pyrazine and 2-cetylpyrazine (Table II). Increases were also generally observed for the PDMS experiment in the presence of NaClO_4 , but they were not as significant as those seen with the CWDVB fiber. In fact, significant decreases in the amount adsorbed were observed for thiazole, pyridine, and acetylpyrazine in the NaClO_4 -PDMS fiber experiment. Thus, from the data generated with NaClO_4 experiments, a universal trend in sorptivity changes of the CWDVB and PDMS fibers cannot be drawn across the compound behaviors seen here.

In contrast, however, with only one exception, the addition of



NaCl to the aqueous solutions resulted in marked increases in sorptivity for both the CWDVB and PDMS fibers (Table II). For example, significant increases due to the presence of NaCl were found for 2,3-dimethylpyrazine and 4,5-dimethylthiazole (Figure 7). For both of these compounds, the presence of NaCl at 0.2 g/mL in the 20-component mixture resulted in increases on the order of 2 in the sorptivity of both fibers. Very similar observations were made for the remainder of the compounds in the CWDVB experiment, except pyrazine. One plausible reason for this finding could be that the capacity of the CWDVB fiber was reached due to the presence of 50 ppm each of the remaining 19 components and their increased adsorption due to the "salting out" effect of NaCl.

Quantitative characteristics

By plotting the concentration of the solutions versus the nanograms adsorbed, an indication of the quantitative characteristics of the adsorption by the PDMS and CWDVB fibers was obtained. Such plots of the performance of the two PDMS and CWDVB fibers toward a solution of thiazole, methylthiazole, dimethylthiazole, ethoxythiazole, and trimethylthiazole are contained in Figures 8 and 9, respectively. For the PDMS fiber, a linear fit to the data seemed appropriate with a regression coefficient (R^2) of 0.997. However, for the CWDVB fiber, a linear fit of the data yielded a lower R^2 value of 0.985. This trend in

more nonlinearity for the CWDVB fiber can possibly be more clearly evident in an actual listing of the FID values from, for example, the thiazole, substituted thiazoles, pyridine, and substituted pyridines (SPME experiments, Table I). Thus, it was apparent that the linear ranges of the two fibers could possibly occur in different concentration ranges for the types of compounds studied here.

To more clearly delineate the linear range of these two fibers and to gain some idea of the detection limits using the approach described herein, a series of experiments using GC-SIM-MSD and GC-TIC-MSD were performed. By performing SPME extractions on a set of serial dilutions in a stock solution containing 50 ppm of each component in a 20-component mixture followed by GC-SIM-MSD, it was possible to collect data in terms of concentration versus average SIM area counts for each component. A selected number of those components, their average TIC area counts, and ions monitored are listed in Table III. Plots of concentration versus TIC area counts for selected concentration ranges revealed some insightful information on the performance of the two fibers. For the CWDVB fiber, a linear curve was found for the concentration range 0.005–0.5 ppm (Figure 10) for all the examined compounds. When the concentration range was extended from 0.005 to 5.0 ppm, the nature of the curve seemed to develop a meaningful change in slope (Figure 11). This change in slope was fully evi-

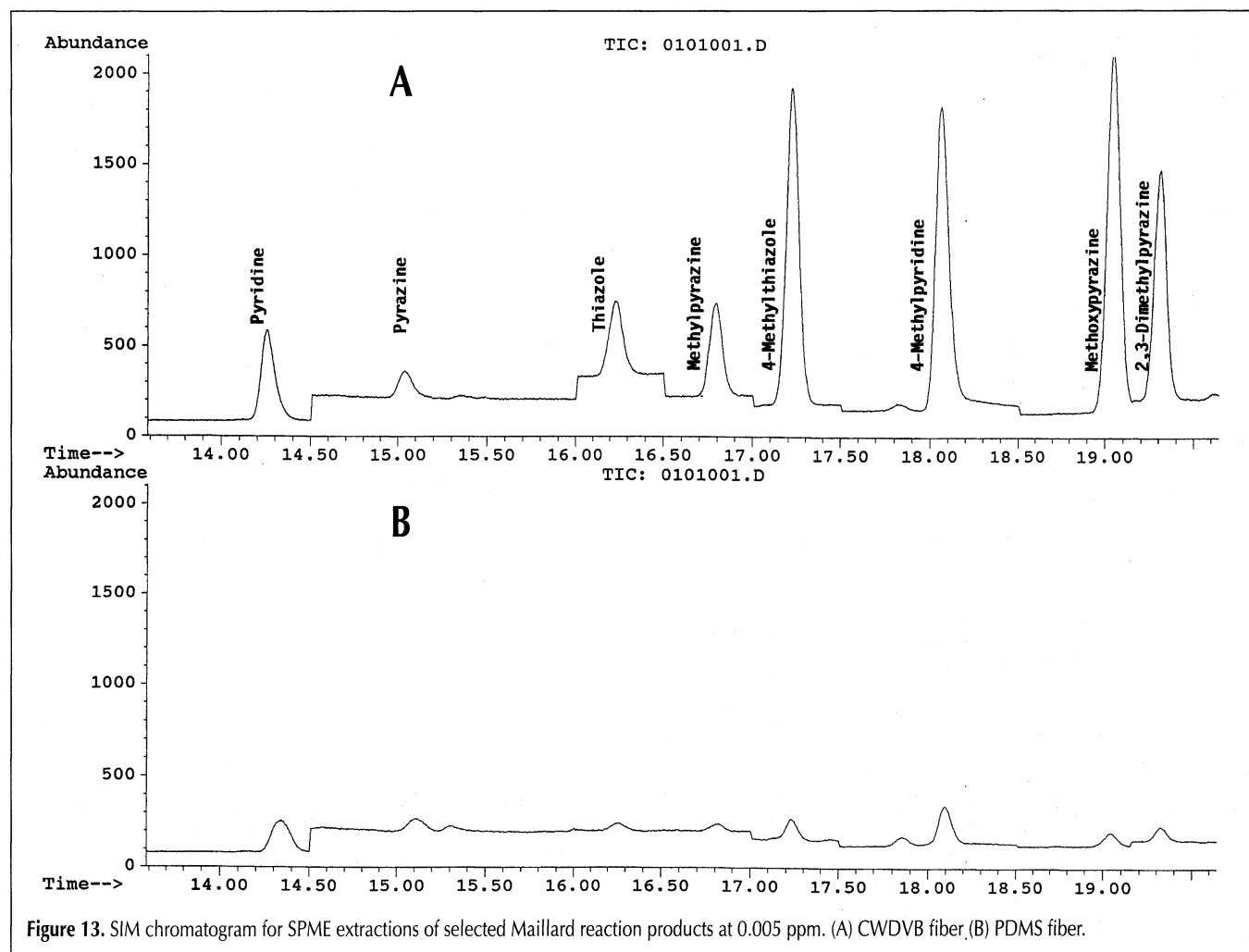


Figure 13. SIM chromatogram for SPME extractions of selected Maillard reaction products at 0.005 ppm. (A) CWDVB fiber. (B) PDMS fiber.

dent when the plot encompassed the range of concentration from 0.005 to 50 ppm (Figure 12). Based on the trends with these curves, it seems quite possible that the capacity of the CWDVB fiber to equally adsorb all of these compound types under these conditions at concentrations greater than 5 ppm is limited. However, under these experimental parameters, an excellent linear response based on SIM values can be obtained over 3 orders of magnitude for these Maillard reaction products by the CWDVB fiber.

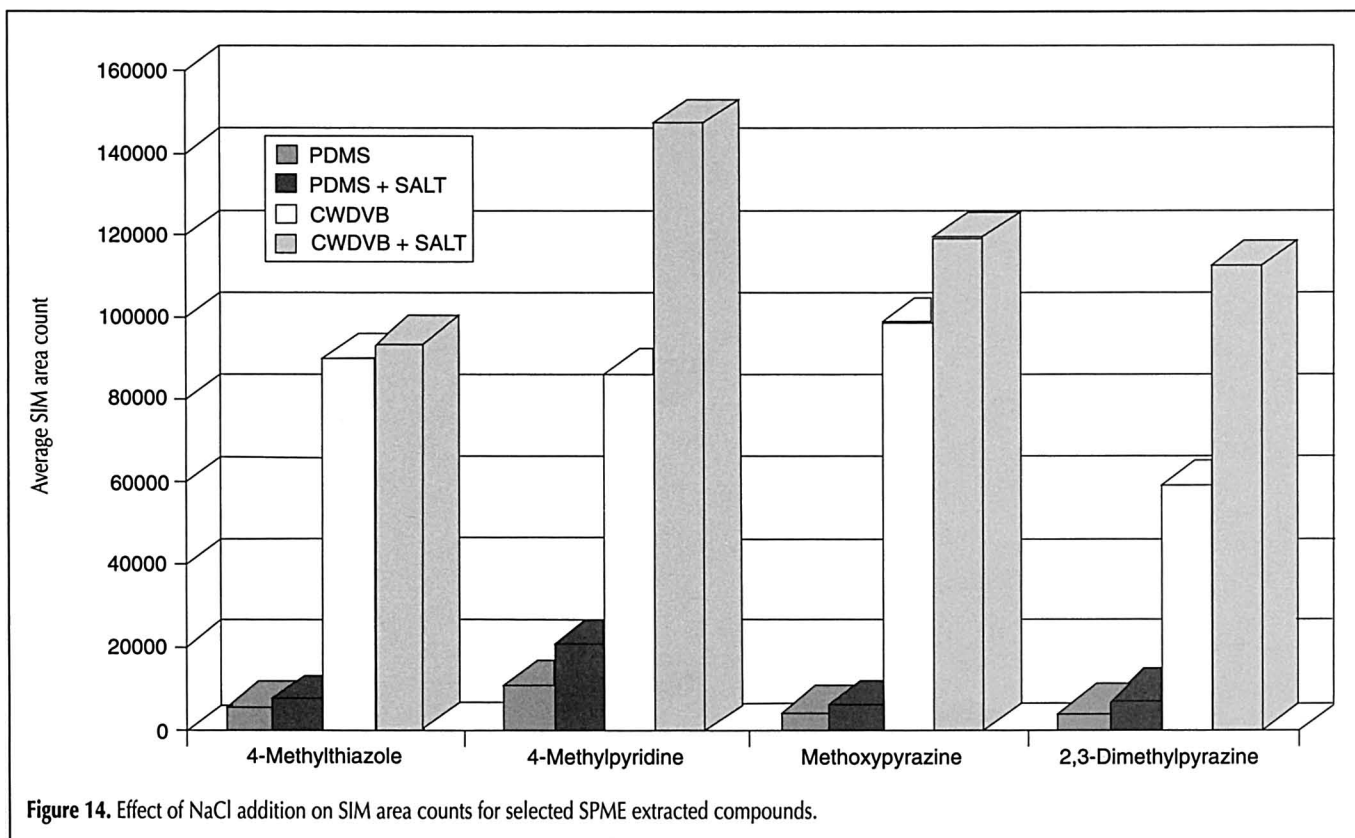
Comparable trends were observed for the PDMS fiber experiments, except that, at the 0.005 ppm concentration, the signal-to-noise ratio and interferences resulted in SIM values that were completely inconsistent with the trend established by solutions containing concentrations greater than 0.050 ppm. This observation is more conveniently illustrated in Figure 13. The top portion of Figure 13 is the SIM chromatogram for the SPME CWDVB extraction of selected Maillard reaction products at 0.005 ppm each, and the bottom portion of Figure 13 is the comparable experiment with the PDMS fiber. It was obvious that the detection limit for the CWDVB fiber was much lower than that for the PDMS fiber. Thus, from a practical perspective for the PDMS fiber, the detection limit would be around 0.050 ppm, whereas the detection limit for the CWDVB fiber can be considered to be around 0.005 ppm for a wide variety of Maillard reaction products dissolved in aqueous solutions.

The addition of NaCl at 0.2 g/mL was shown to alter the amount of adsorbed compound for both fibers. For the majority of cases, increases in the amount of adsorbed compound were found. Thus, it seemed possible that this NaCl "salting out" effect would translate into lower detection limits for these compounds. In support of this, Figure 14 indicates that the SIM area

counts for selected compounds increased significantly in the presence of the NaCl-containing solutions relative to the "salt-free" solutions. Therefore, by coupling the effect of NaCl addition with the very sensitive SIM-MSD analytical approach, the detection limits of this particular SPME approach for these Maillard reaction products could be at or below 1 ppb.

Conclusion

Evidence was presented describing the behavior of two SPME fibers toward aqueous solutions of Maillard reaction products as well as toward the headspace above the aqueous solutions. Relatively short exposures of 10 min to stirring solutions yielded very meaningful insights into the behavior of the CWDVB and PDMS fibers. The relatively polar CWDVB fiber was found to be more selective for the more polar Maillard products when compared with the relatively nonpolar PDMS fiber. Both fibers, however, demonstrated a marked tendency to selectively adsorb the more highly alkyl-substituted components relative to their proton counterparts. By employing GC-SIM-MSD, the detection limit for a number of the Maillard reaction products was found to be well below 5 ppb for both fibers. Addition of NaCl resulted in increased amounts of adsorbed compounds. A linear range of approximately 3 orders of magnitude between 5 and 500 ppb versus selected ion area counts was demonstrated for both fibers. A significant departure from linearity occurred after the 500-ppb concentration was reached, possibly resulting from the capacity limits of the fibers. Notwithstanding, the SPME approach using either a relatively polar fiber, CWDVB, or a relatively nonpolar fiber,



PDMS, is an excellent procedure for the qualitative analysis of Maillard reaction products dissolved in aqueous solutions. To be effective, quantitative analyses using SPME fibers must account for competitive adsorption of components from the sample matrix. By using SIM-MSD, the detection limits of the SPME approach were within the range of unit parts per billion. Such low detection limits are within the range of normal detection limits for aromas by human olfactory sensors. This analytical capability should assist in the development of aroma and flavor formulations.

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