HS–SPME Determination of Volatile Carbonyl and Carboxylic Compounds in Different Matrices

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Abstract

Specific chromatographic methodologies are developed for the analysis of carboxylic acids (C_2–C_6, benzoic) and aldehydes (C_2–C_{10}) of low molecular weight in diverse matrices, such as air, automotive exhaust gases, human breath, and aqueous matrices. For carboxylic acids, the method is based on their reaction with pentafluorobenzyl bromide in aqueous solution, followed by the separation and identification of the resultant pentafluorobenzyl esters by means of headspace (HS)–solid-phase microextraction (SPME) combined with gas chromatography (GC) and electron capture detection (ECD). Detection limits in the µg/m³ range are reached, with relative standard deviation (RSD) less than 10% and linear response ($R^2 >$ 0.99) over two orders of magnitude. The analytical methodology for aldehydes is based on SPME with simultaneous derivatization of the analytes on the fiber, by reaction with pentafluorophenylhydrazine. The derivatization reagent is previously deposited on the SPME fiber, which is then exposed to the gaseous matrix or the HS of the sample solution. The pentafluorophenyl hydrazones formed on the fiber are analyzed selectively by means of GC–ECD, with detection limits in the ng/m³ range, RSD less than 10%, and linear response ($R^2 >$ 0.99) over two orders of magnitude.

Introduction

Carboxylic and carbonylic substances are part of the great variety of organic volatile compounds that may be present in air as contaminants. These substances may be dispersed in the atmosphere from anthropogenic and biogenic primary sources, or they may originate in the atmosphere itself as a result of the different photochemical reactions that all the hydrocarbon-polluting agents can undergo (1). The main sources of carboxylic acids are the oxidation of aldehydes and the reactions of alkenes with ozone. Because of their ample participation in the photochemical reactions of the troposphere and their injurious effects on the atmosphere and human health, the determination of these compounds in air has become important for environmental and work-place safety studies (2–4). The achievement of trace-level detection limits for these polar compounds normally requires sample preconcentration (cryogenic trapping, adsorption on sorbent cartridges, or chemical derivatization) (5). Sampling with sorbents followed by thermal desorption has been employed successfully in the determination of nonpolar contaminants in air. However, the application of this method to the determination of polar compounds is hindered by their strong adsorption and the partial loss of these compounds on the surfaces of injectors and chromatographic columns (5,6). A solution to this drawback has consisted of the combination of chemical derivatization with the use of solid sorbents (3,7). Thus, the most common analytical procedure for the determination of aldehydes and ketones in air involves the circulation of air over a solid sorbent, which has been previously impregnated with 2,4-dinitrophenylhydrazine (8–10). The derivatives are then removed with solvent and quantitated by means of high-performance liquid chromatography (HPLC)–UV, which achieves detection limits in the µg/m³ range. A chlorinated derivatization analogue, 2,4,6-trichlorophenylhydrazine, has been employed with gas chromatography (GC)–electron capture detection (ECD) to achieve detection limits in the sub-µg/m³ range (11), in a procedure that involves sealing the cartridge after sampling and heating it to 100°C for 6 min to perform the derivatization. However, this method requires the addition of an ozone trap to prevent oxidation and deactivation of the derivatization agent. Similar detection limits have been obtained in the GC–MSD quantitation of the oximes formed by the reaction of carbonyls with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) over a polymeric sorbent (Tenax) (3). Cecinato et al. (12) reached parts per trillion by volume detection limits in the determination of carbonyls in air when they utilized silica cartridges impregnated with 2,3,4,5,6-pentafluorophenyl hydrazine (PFPH) to form hydrazones that were extracted in dichloromethane–acetonitrile (4:1) and quantitated with GC–MSD in selected ion monitoring mode.

The most common analytical procedures for carboxylic acids in air and car exhaust include a sampling step with either liquid (potassium hydroxide or calcium hydroxide aqueous solutions) or solid traps (2,13–17). Quartz, glass wool, or cellulose are typical supports used in the latter type of traps to embed potassium

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hydroxide, sodium carbonate, or calcium hydroxide. Potassium-impregnated silica gel-C_{18} cartridges have been employed as well (18,19). These sampling approaches have been combined with various instrumental techniques, such as ion chromatography, liquid chromatography, capillary electrophoresis, and GC (13–19). However, low selectivity, low sensitivity, and long analysis times are common to these procedures. Ion chromatography and GC are the preferred quantitation methods for these analytes, but a sensitive analysis with few interferences requires the introduction of a derivatization step during sample preparation (2,20,21). Sylilation and alkylation are the most common approaches. Ester formation has been achieved by means of reagents such as boron trifluoride–butanol (22–24), boron trifluoride–methanol (13), diazomethane (25,26), pentafluorobenzylbromide (PFBBr) (1), and dibromoacetophenone (13,17).

Solid-phase microextraction (SPME) constitutes an interesting and efficient variation of the trapping–derivatization methods needed for the determination of carbonyls and carboxylic acids in air because it permits the combination of concentration, derivatization, and thermal desorption in a single device. Martos and Pawliszyn employed a polydimethylsiloxane (PDMS)-coated SPME fiber, previously impregnated with PFBHA, for the GC–MSD determination of formaldehyde in air (27). This method showed good agreement with the results of the National Institute of Occupational Safety and Health (NIOSH) method when it was applied in the field and indoors (28). Pan and Pawliszyn (29) and Lee et al. (30) employed diazomethane to derivatize long-chain carboxylic acids after their absorption on PDMS-coated SPME fibers. For low-molecular-weight carboxylic acids, 1-pyrenyldiazomethane was used. It was loaded onto the SPME fiber before its exposition to the sample that contained the carboxylic acids (29). Detection limits in the ng/L to µg/L range were obtained with these methods for the determination of carboxylic acids in aqueous solutions.

This work reports on the development of analytical protocols for the determination of low-molecular-weight carboxylic acids and aldehydes in air, using derivatization to pentafluorophenyl or pentafluorobenzyl analogues, which were quantitated with high selectivity and sensitivity by means of headspace (HS)–SPME and GC–ECD. An on-fiber derivatization SPME–GC–ECD methodology, previously developed in our laboratory for the determination of carbonyls generated during lipid peroxidation (31), was applied to air analysis. Examples of the application of the analytical protocols to the determination of these analytes in diverse matrices (breath, foot sweat, car exhaust, and indoor air at a shoe factory) are included.

Experimental

Reagents and materials

Pentafluorobenzyl bromide, pentafluorophenylhydrazine, butanoic, pentanoic, hexanoic, and benzoic acids, as well as ethanal, propanal, butanal, pentanal, hexanal, octanal, nonanal, and decanal were obtained at 99% or higher purity from Aldrich (Milwaukee, WI). Analytical-grade glacial acetic acid, acetone,

ethyl acetate, and sulfuric acid were purchased from Mallinckrodt (Mexico D.F., Mexico). Propionic acid, sodium chloride, and potassium carbonate were obtained from Merck (Schuchardt, Germany). Zero air (20% O_2 in N_2) and high-purity gases for chromatography were obtained from Aga Fano S.A. (Bucaramanga, Colombia). Fused-silica fibers coated with PDMS (100 µm), poly(acrylate) (85 µm), or PDMS–divinylbenzene (DVB) (65 µm) for use in SPME were purchased from Supelco (Bellefonte, PA). The performance of all three fiber types in the determination of carboxylic acids and carbonyl compounds was compared. Because of their superior retention capacity, the poly(acrylate) and PDMS–DVB coatings were chosen for the carboxylic acid and carbonyl compound determinations, respectively.

Air sampling

Air samples were collected with an M18 VacBag sampler system (SK-M180), together with a gas sampling pump (TBP-102) and 3-L gas sampling Tedlar bags, which were obtained from Apex Inc. Instruments (Holly Springs, NC). A sampling flow of 0.02 L/min during 12.5–15 min was employed in all cases. For carboxylic acid determination, the contents of the Tedlar bag were then bubbled at 0.2 mL/min through two impingers connected in series, each one containing potassium carbonate solution (50 mg/L and 30 mL).

Carboxylic acid determination

Stock solutions of the carboxylic acids (10mM) in acetone were used to prepare individual aqueous solutions of various concentrations (1.27, 2.70, 5.20, 7.20, 10.8, 21.6, 32.0, 43.2, 86.4, and 172.8µM). The derivatization reaction conditions for aqueous solutions of carboxylic acids were adapted from those used by Kawahara (32) with nonaqueous media. Instead of using acetone, as in Kawahara's method, the derivatization reaction was performed directly in aqueous solution. The esters thus formed were extracted by means of SPME rather than with solvent extraction (procedure used in Kawahara's method). Reagent concentration, solution pH, temperature, and reaction time were changed, one at a time, within intervals determined by means of preliminary experiments, in order to determine the conditions that afforded an improved overall esterification yield without increasing its standard deviation. For the standard derivatization conditions selected, the acid solution (9 mL) was transferred to a 12-mL vial where it was mixed with potassium carbonate (1 mL and 0.5 g/L) and a nine-fold excess of PFBBr (430mM in acetone). The vials were sealed, stored at 60°C for 4 h, and, finally, transferred to an ice-water bath for 10 min. This procedure was employed with all of the samples and with the stock solutions to prepare the calibration curves for the HS–SPME–GC–ECD analysis. Quadruplicate injections of an equimolar mixture of the carboxylic acid derivatives obtained by this procedure showed relative standard deviations (RSDs) below 0.5% for their retention times.

Poly(acrylate)-coated (85 µm) SPME fibers were used to sample the pentafluorobenzyl esters of the carboxylic acids formed in aqueous solution by reaction with PFBBr. The sampling conditions were established after a comparative study of the amount of PFBBr derivatives extracted when the solution pH (3,7,9), ionic

strength (0, 100, 150, 200 g/kg NaCl), extraction temperature (30°C, 40°C, 60°C), and time (20, 30, 40, 80 min) were varied systematically. The extraction was performed by exposure of the fiber to the HS of the magnetically stirred (900 rpm) aqueous solution (2 mL) in 5-mL vials for 40 min at 30°C, after addition of NaCl (200 g/kg) and pH adjustment (pH = 7).

Aldehyde determination

The procedure described by Stashenko et al. (33) was employed to prepare hydrazone derivatives of the individual aldehydes. A PFPH methanolic solution was reacted with a 50% stoichiometric excess of each one of the carbonyl compounds. The resulting derivatives were used to prepare hidrazone solutions of 1.0, 2.5, 5.0, 10.0, 20.0, 30.0, 40.0, and 60.0μM, which were used for the external calibration and the identification of the analytes of interest by comparison of their retention times with those of the standards.

The gaseous aldehyde standards were prepared using volumetric injection. A measured amount of an aldehyde standard (C_2–C_{10}) was deposited in a Tedlar bag, which contained 3 L of zero air, through the septum that these bags have using a microsyringe (0.1–1.0 μL). After the sample was prepared, the needle of the SPME syringe was inserted through the septum, immediately exposing the PDMS–DVB coating to the analytes. After 30 min, the fiber was withdrawn and inserted in the injection port of the GC. The air samples were collected in 3-L Tedlar bags and analyzed following the same procedure.

Chromatographic analysis

Sample analysis was carried out in an HP-5890A Series GC (Hewlett-Packard, Palo Alto, CA) equipped with split/splitless injection and ECD (^{63}Ni-ECD). The chromatographic data were processed with HP ChemStation A.06.03 software (Hewlett-Packard). The chromatographic column was a DB-5 (J&W Scientific, Folsom, CA) fused-silica capillary column coated with 5% phenyl poly(dimethylsiloxane) (30 m × 0.25-mm i.d., with 0.25-μm d_f). Helium (99.995%) was used as the carrier gas (1 mL/min) with a column inlet pressure of 90 kPa. An argon–methane (9:1 v/v) mixture was used as the auxiliary gas in the detection system at 60 mL/min. The oven temperature was programmed from 60°C (2 min) to 250°C (2 min) at 8°C/min for the analysis of the acid derivatives and from 120°C to 250°C (4 min) at 8°C/min for the hydrazone derivatives. The injector and

detector temperatures were maintained at 250°C and 270°C, respectively. The split ratio was 10:1.

Mass spectra (electron impact at 70 eV) were obtained with an HP-5890A Series II GC coupled to an HP 5972 MSD, equipped with a split/splitless injector (split 1:30) and a data system (HP ChemStation) with NBS75K and Wiley 138K mass spectra libraries (John Wiley & Sons, NY, New York). An HP-5MS 50-m × 0.25-mm (i.d.) capillary column coated with 5% phenyl poly(methylsiloxane) (0.25-μm film thickness) was used. The GC oven was programmed from 60°C (2 min) to 250°C (2 min) at 8°C/min. The temperatures of the ionization chamber and of the transfer line were 185°C and 285°C, respectively. Mass spectra and reconstructed chromatograms were obtained by automatic scanning in the mass range m/z 40–350 at 3.5 scan/s.

Results and Discussion

Analytical methods

The analytical methods employed in this work to determine carboxylic acids and carbonyl compounds at low concentrations were designed to obtain high sensitivity and selectivity and to include as few steps as possible, in order to make them swift and to decrease the likelihood of cross contamination and analyte loss. The analytes were converted into their pentafluorophenyl or pentafluorobenzyl derivatives in order to obtain high sensitivity with the ECD, which in turn reduces the amount of sample required for the analysis. The use of SPME for on-fiber derivatization of aldehydes or for HS–SPME sampling of the PFBBr carboxylic acid derivatives formed in slightly acidic aqueous solution eliminated the steps of solvent extraction and concentration under nitrogen, common to many existing analytical methods.

For the determination of carboxylic acids in air, the sample may be collected in the field and brought to the laboratory in Tedlar bags, or it could be bubbled directly into 2- × 30-mL potassium carbonate (50 mg/L) solutions. The partial ionization of the carboxylic acids under these conditions diminishes losses because of volatilization. The recovery calculated after derivatization and HS–SPME was near 80% for acetic and hexanoic acids and higher than 99% for acids of 3-, 4-, and 5-carbon atoms. However, it was very low (6%) for benzoic acid, but the derivatization and HS–SPME extraction showed relatively similar yields for all carboxylic acids examined, and the trapping in aqueous solution showed lower recoveries for benzoic acid caused by condensation losses because of its lower volatility (boiling point = 249°C), relative to the other carboxylic acids examined (for hexanoic acid, boiling point = 205°C). Thus, the recovery calculated for the method, excluding the trapping step (bubbling through potassium carbonate solution), shows high values for all carboxylic acids studied (Table I). The calibration curves and response factors for each analyte were calculated from the chromatograms obtained by means of HS–SPME and GC–ECD for esters formed from standard acid solutions of different concentrations. Table I contains the calibration curve results for the determination of carboxylic acids in air. Sub-μg/m^3 quantitation limits were reached for all carboxylic acids examined, and the linearity of the calibration curves presented R^2 values above 0.99 in all cases.

Table I. Calibration Data for the Determination of Carboxylic Acids in Air

Carboxylic acid	LOD (μg/m^3)	LOQ (μg/m^3)	R^2	Recovery (%) Overall	Recovery (%) From aqueous trap
Ethanoic	20.16	40.32	0.9994	86	97.2
Propanoic	11.56	23.11	0.9961	97	94.8
Butanoic	25.38	50.75	0.9986	100.2	98
Pentanoic	36.77	73.53	0.9968	100.0	98
Hexanoic	105.94	211.88	0.9965	88	95.9
Benzoic	271.11	542.21	0.9965	6.5	92.4

The identity of the PFBBr carboxylic acid derivatives was confirmed by MS. Their mass spectra contained molecular ions with relatively low abundances (1–32%), which is in agreement with the observations made by Brill (34), who found abundances between 1% and 20%. The base peak in all of the mass spectra of the PFBBr derivatives was found at *m/z* 181, assigned to the $[C_6F_5CH_2]^+$ ion. It was accompanied by a signal at *m/z* 161, corresponding to a loss of HF from the pentafluorobenzyl fragment.

Aldehyde determination by on-fiber derivatization with PFPH has been showed to permit femtogram-level detection limits (31,33). The method previously developed in our laboratory was applied to the air samples contained in Tedlar bags. Synthetic air samples containing known amounts of aldehydes were used to determine the fiber exposure time and PFPH load amounts most appropriate to the analyte levels examined. These samples were also employed to construct the calibration curves (Table II). Very good linearity ($R^2 > 0.99$) was achieved for all the aldehydes studied, and their quantitation levels were in the sub-ng/m³ range.

The novelty of the methods applied in this work to the determination of polar contaminants in diverse sample matrices resides in the particular conjugation of rather simple setups, a smaller number of steps, shorter experimental time, and lower environmental impact (negligible solvent consumption) to achieve high selectivity and sensitivity. These advantages result primarily from the combination of SPME sampling with derivatization and chromatographic electron capture detection.

Applications

Aldehydes at a shoe factory

The air in the main floor of a local footwear factory (Bucaramanga, Colombia) was sampled in two areas that corresponded to two distinct manufacturing operations. In area 1, the leather pieces are mounted and glued around the shoe frameworks, and edges are burned off. In area 2, outsoles are lacquered, and cleaning agents are applied to remove impurities and provide luster to the leather. All eight aldehydes were detected at concentrations that could cause allergies and discomfort to the workers. In contrast, a duplicate determination of aldehydes in air from a pedestrian sidewalk at our university campus did not detect any of these aldehydes at concentrations above the method's detection limit. Air sampling (two Tedlar bags per site) was performed on a Friday afternoon, at the end of the working day (5 p.m.) and week. Table III contains the aldehyde concentrations found in the air at the two sampled factory sites. However, the NIOSH-recommended time-weighted average exposure limits for acetaldehyde (324 mg/m³) and pentanal (175 mg/m³) were above the concentrations determined at the footwear factory. Currently, there are no NIOSH recommended limits for workplace exposure to the other aldehydes studied (35).

Aldehydes and carboxylic acids in car exhaust

The exhaust fumes from two compact cars with 4-cycle combustion engines, with and without catalytic converter, were sampled by means of a 1-m stainless steel tube (0.8-mm i.d.) inserted 10 cm into their exhaust pipes. The stainless steel tube was connected to the air sampling Tedlar bag by means of Teflon tubing

Table II. Calibration Parameters for the Determination of Aldehydes in Air

Aldehyde	LOD (ng/m³)	LOQ (ng/m³)	R^2	Recovery (%)
Ethanal	0.111	0.222	0.9989	98
Propanal	0.129	0.257	0.9983	98
Butanal	0.128	0.256	0.9983	98
Pentanal	0.151	0.302	0.9980	98
Hexanal	0.160	0.320	0.9989	98
Octanal	0.036	0.073	0.9979	98
Nonanal	0.035	0.069	0.9980	99
Decanal	0.298	0.596	0.9968	99

Table III. Concentration of Aldehydes in Air at Two Sections of a Footwear Factory

	Concentration (ng/m³)*	
Aldehyde	Site 1	Site 2
Ethanal	54 ± 4.3	53 ± 1.2
Propanal	58 ± 1.7	103.3 ± 0.93
Butanal	9.8 ± 0.37	7.2 ± 0.21
Pentanal	15 ± 1.1	15.4 ± 0.66
Hexanal	12 ± 1.1	13.2 ± 0.37
Octanal	10 ± 1.1	8.0 ± 0.26
Nonanal	11.0 ± 0.84	13.4 ± 0.20
Decanal	34 ± 2.4	25.8 ± 0.50

* Average concentration ± s (*n* = 2).

Table IV. Concentration of Carboxylic Acids and Aldehydes Found in Car Exhaust Gases

	Concentration (mg/m³)*	
Acid	Without catalytic converter	With catalytic converter
Acetic	43.6 ± 0.90	5 ± 3.1
Propanoic	6.2 ± 0.17	0.0 ± 0.1
Butanoic	8.8 ± 0.25	0.053 ± 0.0063
Pentanoic	0.217 ± 0.0070	0.18 ± 0.017
Hexanoic	0.20 ± 0.011	0.045 ± 0.0045
Benzoic	2.10 ± 0.070	0.274 ± 0.0022
Aldehyde	Concentration (ng/m³)*	
Ethanal	800 ± 140	430 ± 15
Propanal	170 ± 20	160 ± 19
Butanal	100 ± 14	54.1 ± 0.81
Pentanal	250 ± 25	100 ± 1.5
Hexanal	33 ± 3.4	73 ± 2.5
Octanal	15.2 ± 0.85	47 ± 5.0
Nonanal	110 ± 16	12 ± 1.8
Decanal	64 ± 5.0	19 ± 3.1

* Average concentration ± s (*n* = 2).

sufficient in length (6 m) to cool down the air before its admission into the sampling bag. The Teflon tubing also served to trap most of the particulate matter released by the car without a catalytic converter, which formed a dark deposit on the tubing walls. Very few particulates reached the bag, but none reached the impingers used to trap the carboxylic acids. The car with a catalytic converter did not release particulate matter. Table IV shows the concentrations of aldehydes and carboxylic acids found in duplicate samples taken from the car exhausts. The NIOSH-permissible exposure limits (8-h time-weighted averages) for acetic, propanoic, and pentanoic acids were 25, 30, and 176 mg/m^3, respectively (36). The C_3 and C_4 carboxylic acids were the species most effectively reduced by the catalytic converter, and the acetic acid emissions were practically the same in both types of cars sampled. Figure 1 presents chromatographic profiles for the PFBBr ester derivates of carboxylic acids in an aqueous solution and in the exhaust fumes from the car without a catalytic converter. On the other hand, all aldehydes examined were found at a lower concentration in the exhaust from the car with a catalytic converter.

Carboxylic acids in foot sweat

During a separate forensic research project conducted in our laboratory, five male volunteers were asked to wear sport shoes for 8 h and a cotton-gauze insole within their socks, maintained in close contact with their feet by means of plastic wrap. After the insole was collected from the volunteers, it was cut into 2-cm strips. A weighed strip was transferred to a 25-mL flask and extracted with HPLC-grade water (25 mL) for 1 h at room temperature. An aliquot (9 mL) of this extract was subjected to the PFBBr derivatization and HS–SPME sampling procedure described in the Carboxylic acid determination section. Table V shows that acetic, propionic, and benzoic acids were the most abundant carboxylic acids in the volunteers' foot sweat. Volunteers presented concentration profiles that differed mainly
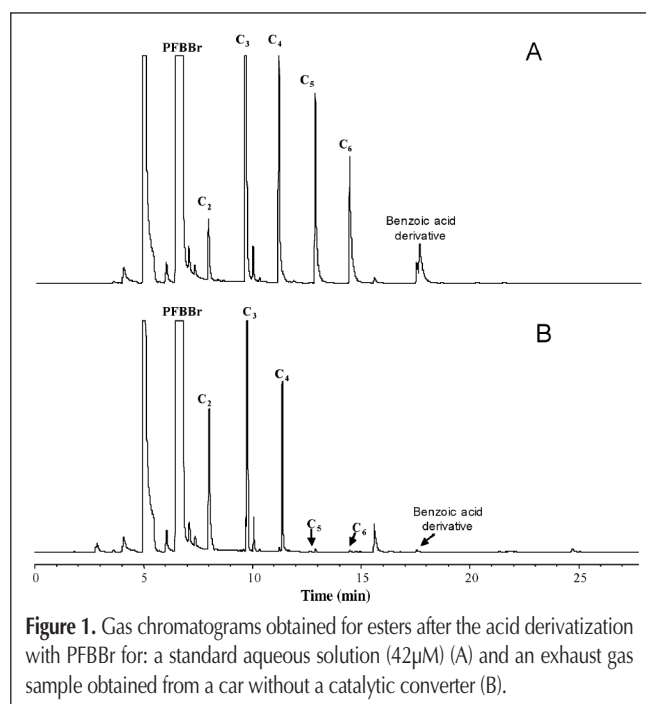
in the concentrations of acetic and propionic acids, which varied by factors of up to three-fold. Blanks of the shoes, talc, cotton insole, and aqueous solution employed in the extraction of the insole revealed the presence of small amounts of esters of acetic and propionic acids as contaminants of the derivatization reagent. Benzoic acid (40 mg/kg) was found in the aqueous extract (100 mL, 37°C) of the sport shoe employed in the study. This indicates that the shoe materials contributed to the benzoic acid determined in the volunteer's foot sweat. However, GC–MS studies have documented the presence of benzoic acid among 346 different compounds collected from human skin emanations (37–39). Indeed, samples of foot sweat from volunteers who used talc showed a 60% decrease in benzoic acid concentration. Thus, the benzoic acid determined in foot sweat samples resulted from metabolism and contributions from the shoe materials.
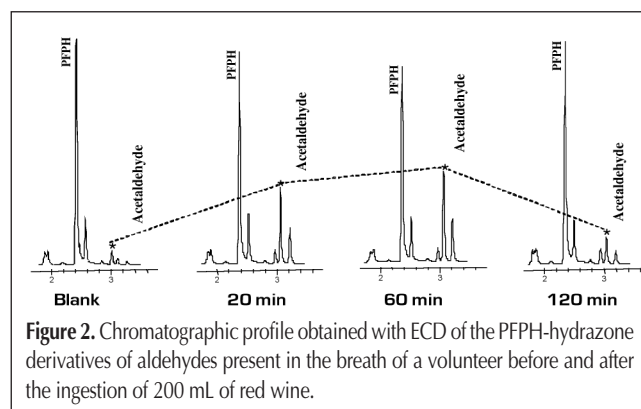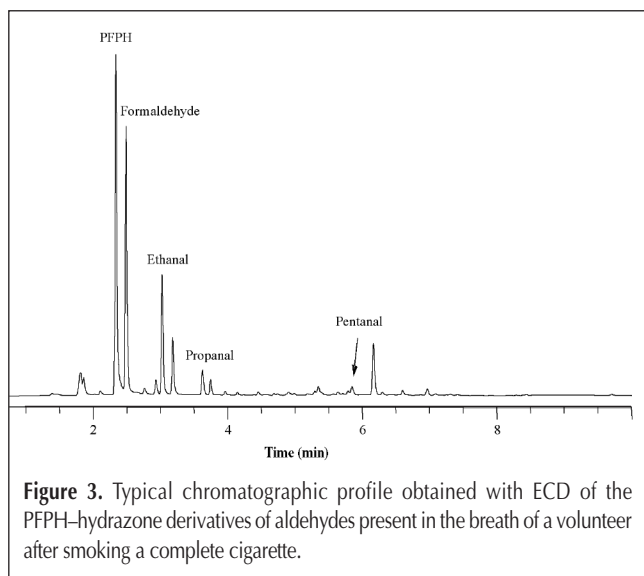
Breath analysis

The on-fiber derivatization method was used for the HS–SPME–GC–ECD determination of aldehydes in human breath. SPME breath sampling was performed with a device in which the SPME holder was attached to the end of a glass tube equipped with a side arm, similar to that employed by Grote and Pawliszyn (40). After placing the other end of the glass tube in their lips, volunteers held their breath for 10 s and then slowly released it through the glass tube and over the PFPH-loaded SPME fiber for 50 s. The procedure was repeated five times, for a total period of 10 min.

The PFPH-loaded PDMS–DVB (65 μm) SPME fiber was exposed (10 min) to the breath of individuals before and after smoking or

Figure 1. Gas chromatograms obtained for esters after the acid derivatization with PFBBr for: a standard aqueous solution (42μM) (A) and an exhaust gas sample obtained from a car without a catalytic converter (B).

Table V. Concentration of Low-Molecular-Weight Carboxylic Acids Found in Foot Sweat from Five Male Volunteers

Volunteers	Carboxylic acid concentration (mg/kg)					
	C_2	C_3	C_4	C_5	C_6	Benzoic
A	432.1	46.4	1.6	2.6	2.6	7.4
B	585.8	41.7	1.2	2.0	1.3	15.3
C	233.1	96.4	1.1	1.3	0.9	24.4
D	460.9	28.3	1.1	2.0	1.2	19.7
E	256.7	87.3	0.1	0.0	0.3	22.1

Figure 2. Chromatographic profile obtained with ECD of the PFPH-hydrazone derivatives of aldehydes present in the breath of a volunteer before and after the ingestion of 200 mL of red wine.

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Figure 3. Typical chromatographic profile obtained with ECD of the PFPH–hydrazone derivatives of aldehydes present in the breath of a volunteer after smoking a complete cigarette.

wine consumption. Figure 2 shows the variation of the chromatographic profile as a function of time after the ingestion of 200 mL of red wine. The crest in acetaldehyde released at 60 min agrees with the known ethanol metabolic process in the human body. Figure 3 contains a typical chromatographic profile of the breath of a volunteer after smoking a full cigarette. Methanal, ethanal, propanal, and traces of pentanal were detected. Because the derivatives are obtained as the E and Z isomers, the most intense peak of each pair was used for quantitation purposes.

Carboxylic acids in rain

Two combined samples were formed with 50-mL rain water samples collected at five spots that corresponded with the corners and the center of a 100-m square. The combined samples were subjected to the PFBBr derivatization procedure (see Carboxylic acid determination section) and the chromatographic analysis of the derivatives thus formed showed that acetic acid was the single carboxylic acid present, at a concentration of $113 \pm 8.3 \mu M$.

Conclusion

The analysis methods employed in this work were based on the combination of SPME sampling with the derivatization of low-molecular-weight carboxylic acids or carbonyl compounds to pentafluorophenyl or pentafluorobenzyl analogs to form simple analytical procedures with few steps and solvent-free extraction with no evaporation routines. The minimum levels of detection (signal-to-noise = 5) of the method for carboxylic acids were between 0.028 and 0.0185 μM for aqueous matrices and between 20.16 and 271.1 $\mu g/m^3$ for gaseous matrices. The analysis of aldehydes in air reached detection limits in the ng/m^3 range. The use of Tedlar bags in combination with SPME constitutes a very fast, simple, and reproducible technique for monitoring VOCs. The examples presented in this work illustrate the easy and diverse applications of these solvent-free, clean, and highly sensitive methodologies to various fields of research.

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