

# Environmental and biological determination of acrolein using new cold fiber solid phase microextraction with gas chromatography mass spectrometry

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**Abstract** Acrolein is a pollutant released daily to the indoor environment from different sources. The present study reports the development of a simple and sensitive cold fiber solid phase microextraction sampling method for the determination of acrolein in exhaled air and indoor air by gas chromatography mass spectrometry. O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine was used as derivatizing agent supported on a 65- $\mu\text{m}$  polydimethylsiloxane-divinylbenzene SPME fiber. An acrolein permeation tube at 326.25  $\text{ng min}^{-1}$  rate was used to generate gaseous standards. The method shows good results for main validation parameters. The limits of detection and quantification were 2.88 and 5.08  $\mu\text{g m}^{-3}$ , respectively, for indoor analysis; and 2.40 and 3.79  $\mu\text{g m}^{-3}$ , respectively, for exhaled air analysis. The precision showed standard deviation ranges from 6.00 to 8.00% for intra-assay analyses and from 8.00 to 10.00% for inter-assay analyses. After optimizing the conditions, analyses of real samples were performed on indoor environments contaminated by cigarette smoke, or heated oil, including pastry shops, restaurants, churros stands, and closed parking cars located in the city of Belo Horizonte, Brazil. Acrolein breaths of exposed people were also determined. A good Pearson correlation coefficient ( $r = 0.901$ ) was observed between the concentration of acrolein in indoor air and exhaled air, allowing to propose acrolein breath as environmental exposure biomarker.

**Keywords** Acrolein · Cold fiber SPME · Indoor · Exhaled air

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## Introduction

Acrolein (2-propenal) is a pollutant introduced daily to the environment from many sources, such as cigarette smoke, forest fires, heated oil, or released indoor from decorative items, construction materials, carpets, wood coatings, glues, adhesives, and inks [1, 2]. It is also produced by the oxidation of atmospheric chemicals such as 1,3-butadiene [3], a hydrocarbon present in vehicle exhaust [3, 4]. Besides, the great Brazilian use of oxygenated fuels become quite significant the amount of acrolein emitted by motor vehicles [5].

Acrolein is toxic to humans via all administration routes including inhalation, ingestion, or skin absorption. It is mainly considered a serious irritant to the respiratory system. In acute exposure (short term), it can induce asthma, especially in children, and decrease lung functions in the elderly [1, 6]. Most of the damaging acrolein effects result from its highly corrosive and irritant properties; its contact can cause necrosis of the skin or eyes. Recently, acrolein is associated with deregulation of glucose transport, diabetes, and insulin resistance [7]. In addition, there are already reports of chemical modifications of RNA induced by short-term exposure to air contaminated by acrolein [8]. However, acrolein is not considered carcinogenic to humans (Group 3) [9] since existing animal cancer data are considered inadequate to determine its acrolein carcinogenicity [10].

Considering the adverse effects to human health produced by acrolein, different global legislation has been established to control the environmental acrolein levels [11]. The American Conference of Governmental Industrial Hygienists (ACGIH) recommended a Threshold Limit Value (TLV) of 250  $\mu\text{g m}^{-3}$ . The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) and Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) are also of 250  $\mu\text{g m}^{-3}$ . The

Environmental Protection Agency (EPA) inhalation reference concentration (RfC) is  $0.02 \mu\text{g m}^{-3}$ . In Brazil, occupational exposure limit values for acrolein were not established.

Acrolein risk assessment can be performed by monitoring the ambient air and through biological monitoring using biomarkers.

Acrolein biological monitoring can be achieved through different methods. The quantification of acrolein-protein adducts (APA) in serum has been proposed as biomarker since acrolein participate of addition reactions with proteins. The macromolecule glucose-6-phosphate dehydrogenase (G6PD) is also used as a biomarker of acrolein exposure due to its possible formation of an adduct with lysine in blood [1]. However, since collection of blood is invasive, it is easier to analyze urine metabolites in bio monitoring studies. The main compounds used as acrolein metabolite excreted in urine are 3-hydroxypropyl mercapturic acid (3-HPMA) and *N*-acetyl-S-(2-carboxyethyl)-L-cysteine (CEMA) [12]. Nonetheless, urine collection method has its limitations, urinary biomarkers require the simultaneous determination of creatinine concentration to account urine dilution, which can vary throughout each day. Finally, the determination of acrolein and other aldehydes in exhaled breath condensed (EBC) showed that EBC acrolein level was clearly higher for smokers [13].

Environmental analysis of acrolein requires efficient sampling and determination methods being an analytical challenge due to acrolein characteristics of low molecular weight, high polarity, high reactivity, and self-polymerization capacity.

Acrolein air sampling methods have been proposed recently and used cartridge with sorbents such as 2,4-dinitrophenylhydrazine-coated Florisil [14], pentafluorophenyl hydrazine (PFPH) [15], or dansylhydrazine (DNSH) [16]. However, these methods present some applicability limitations such as the use of pumps, inadequate sensitivity, and poor reproducibility.

Solid phase microextraction (SPME) can be a good option to sampling acrolein [17–19], since it is a solvent-free method that integrates sampling, isolation, and concentration; besides, it presents rapid and simple sampling. Acrolein SPME analysis involves on-fiber derivatization using *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) derivative and gas chromatography coupled to mass spectrometry (GC/MS) analysis [17]. In-tube solid phase microextraction (IT-SPME) using 2,4-dinitrophenylhydrazine (DNPH) derivatization has been used for acrolein analysis by liquid chromatography using diode array detection (LC-DAD) [18]. Despite carbonyl compounds analysis by LC presents good robustness and repeatability, GC has the advantage of furnishing good separation from complex matrices and high sensitivity.

The aim of the present study was the development of new method for acrolein sampling in environmental and breath air using cold fiber solid phase microextraction (CF-SPME) with

determination by GC/MS. The CF-SPME method used lower fiber temperature to restrict the exothermic magnitudes of SPME and thus increases the fiber sorption capability. It was used on-fiber derivatization with PFBHA forming thermally stable oxime adducts that was analyzed by GC/MS. The developed method was applied to the determination of acrolein in air contaminated with cigarette smoke, burning of oil used in the preparation of foods, and vehicle exhaust gases. Furthermore, the method was also used for determination of acrolein in breath air of people staying in a room exposed to tobacco smoking. The correlation between the concentration of acrolein in indoor air and exhaled air was also assessed.

## Materials and methods

### Reagents and supplies

Ultra-pure water was obtained from Elga Pure lab Classic (Cotia, SP, BR), helium and synthetic air with 99.999% purity were purchased from Air Liquid (Contagem, MG, BR), derivatizing reagent PFBHA from Fluka (Campinas, SP, BR).

### GC/MS system

A Thermo Electron Trace gas chromatograph system coupled to a Polaris Q ion trap mass spectrometer from Thermo Scientific (West Palm Beach, FL, USA) was used. The GC was equipped with a capillary column ( $30 \text{ m} \times 0.25 \text{ mm id} \times 0.25 \mu\text{m film}$ ) containing 5% diphenyl, 95% dimethylpolysiloxane, from Agilent Technology Inc. (Santa Clara, CA, USA). Chromatographic analysis was performed in the splitless mode for 1 min using injector temperature at  $215 \text{ }^\circ\text{C}$  and helium flow rate of  $1.5 \text{ mL min}^{-1}$ . The oven temperature program started at  $45 \text{ }^\circ\text{C}$ , was held for 1 min, raised to  $200 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C min}^{-1}$ , raised to  $290 \text{ }^\circ\text{C}$  at  $70 \text{ }^\circ\text{C min}^{-1}$ , and held for 2 min. The total run time was 11 min. The mass spectrometry used ionization impact electron mode with energy of 70 eV, where the ion source temperature was  $250 \text{ }^\circ\text{C}$  and the GC/MS interface was  $300 \text{ }^\circ\text{C}$ . Analysis was performed in the full scan mode ( $50\text{--}650 \text{ m/z}$ ), and for quantification, it used the  $m/z$  fragments 181, 250, and 432.

### Derivatization procedure

A  $65\text{-}\mu\text{m}$  polydimethylsiloxane-divinylbenzene (PDMS/DVB) from Supelco (Bellefonte, PA, USA) fiber was selected for the analysis because it presents better results than all the other fibers tested (PA, PDMS, CAR/PDMS/DVB). Prior to use, the PDMS/DVB fibers were conditioned according to the manufacturer's instructions, they were immersed in 10 mL of ultra-pure water solution containing

175  $\mu\text{L}$  of ethanol during 1 h under constant stirring, and then heated during 30 min at 250  $^{\circ}\text{C}$ . One milliliter of the derivatizing solution at 17.0  $\text{g L}^{-1}$  concentration was placed in a 5-mL glass vial which was sealed with Teflon septum and aluminum caps. The fiber was then exposed to the headspace of the derivatizing solution. The fiber headspace exposure times of 10, 20, 40, and 60 s were tested. Agitation was used to facilitate the diffusion process of the derivatizing PFBHA to the fiber. Speeds of 645 and 1470 rpm were tested as well. After derivatization, the fiber was gathered and brought directly to the sample bulb of the standard gas generator.

### Standard acrolein generation with permeation tubes

The system used for generating standard gases, shown in Fig. 1, was developed in our laboratory [20]. It was equipped with an acrolein permeation tube of 3.5 cm long having permeation rate of 326.25  $\text{ng min}^{-1}$  at 30  $^{\circ}\text{C}$ , purchased from Vici Metronics (Poulsbo, WA, USA) and certified for traceability by NIST standards. This tube was subjected to a constant flow with temperature controlled by a thermostat at  $30.0 \pm 0.1$   $^{\circ}\text{C}$ .

The concentrations of acrolein were calculated from the expression:

$$C = 10^3 \times Q / F$$

where  $C$  ( $\mu\text{g m}^{-3}$ ) is the concentration of acrolein at 101.3 kPa and 298 K,  $Q$  ( $\text{ng min}^{-1}$ ) is the permeation rate, and  $F$  is the corrected flow ( $\text{mL min}^{-1}$ ) at 101.3 kPa and 298 K. For each concentration level of the analytical curves, the flow was altered, and after the 15 min equilibrium time, the flow was measured in replicate ( $n = 7$ ). The dilutions required for the

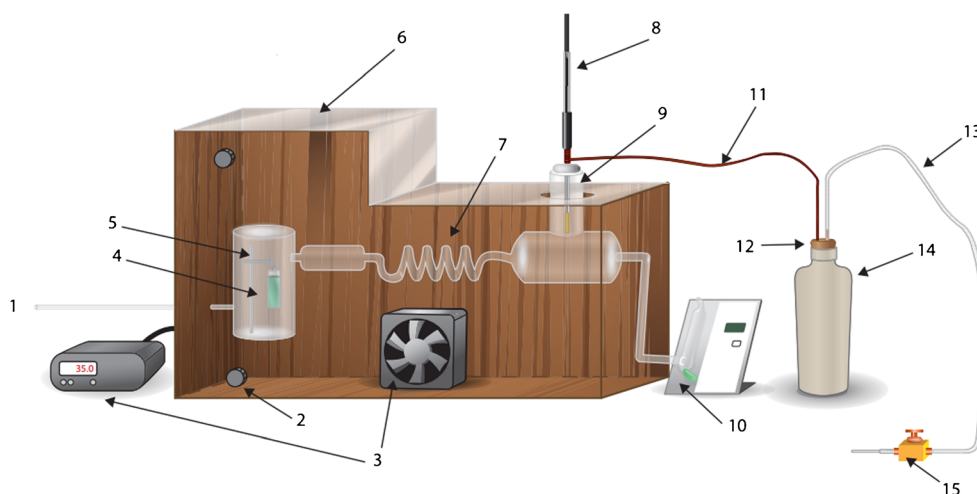
analytical curve construction were obtained through the control of airflow in the permeation chamber. The blank analyzes were obtained after withdrawing the permeation tube and passing diluent air for 24 h before performing the extraction.

### CF-SPME method

The extraction method was performed by SPME using a cold fiber system developed in a previous study [21]. The cooling device was used to cool the fiber immersed in the sample bulb of the standard gas generator. The fiber exposure time in the sample bulb was 15 min following the National Institute for NIOSH methodology for a short-term exposure limit (STEL) [22]. Besides, the breath-sampling period was 30 s that did not cause volunteers respiratory discomfort. The procedure that allowed collecting the alveolar portion of expiration was as follows: inhalation through noses following held breath for about 5 s; then, exhalation for approximately 5 s without the presence of the SPME fiber; and finally, exhalation as slowly as possible directly onto the exposed CF-SPME fiber during 30 s. After collection periods, the fiber was transferred to the GC injector for thermal desorption.

### Sample collection

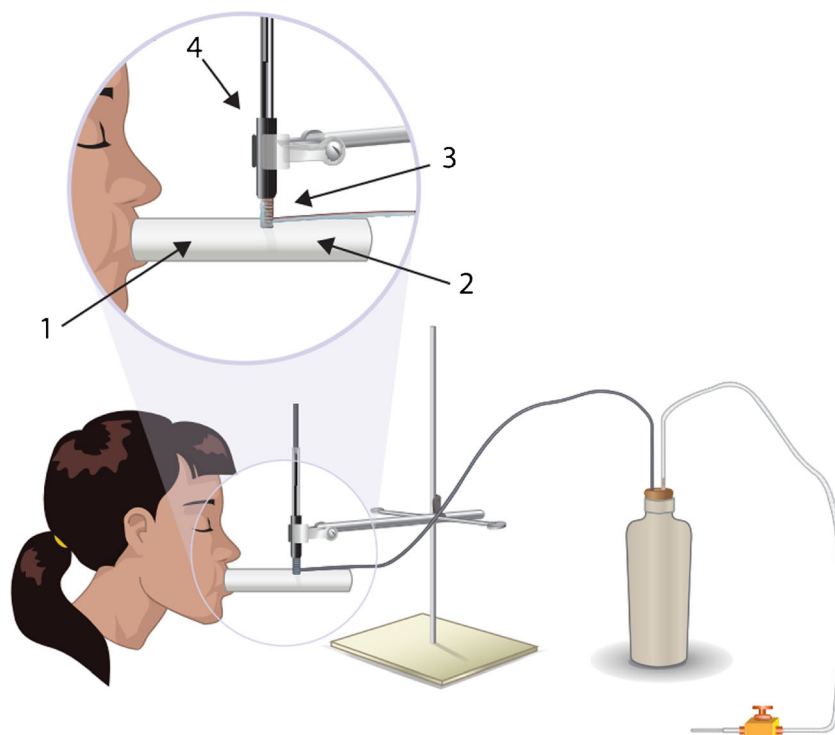
Acrolein sampling in ambient and exhaled air was conducted in June and July of 2015, when the average temperature was  $22 \pm 3$   $^{\circ}\text{C}$ . The selected sampling points in the Brazilian city of Belo Horizonte ( $19^{\circ} 55' 57''$  S,  $46^{\circ} 56' 32''$  W) considered the



**Fig. 1** Schematic for the device for vapor generation: 1—tube from synthetic air cylinder; 2—flow control valve; 3—temperature control system with resistance and small fan; 4—permeation tube from VICI Metronics; 5—permeation chamber; 6—heat insulator; 7—

homogenization chamber; 8—CF-SPME fiber; 9—sampling bulb; 10—digital flow meter; 11—copper tube (i.d. 1.6 mm); 12—stopper; 13—rubber hose (i.d. 5.0 mm); 14—dewar flask; 15—cooling system valve

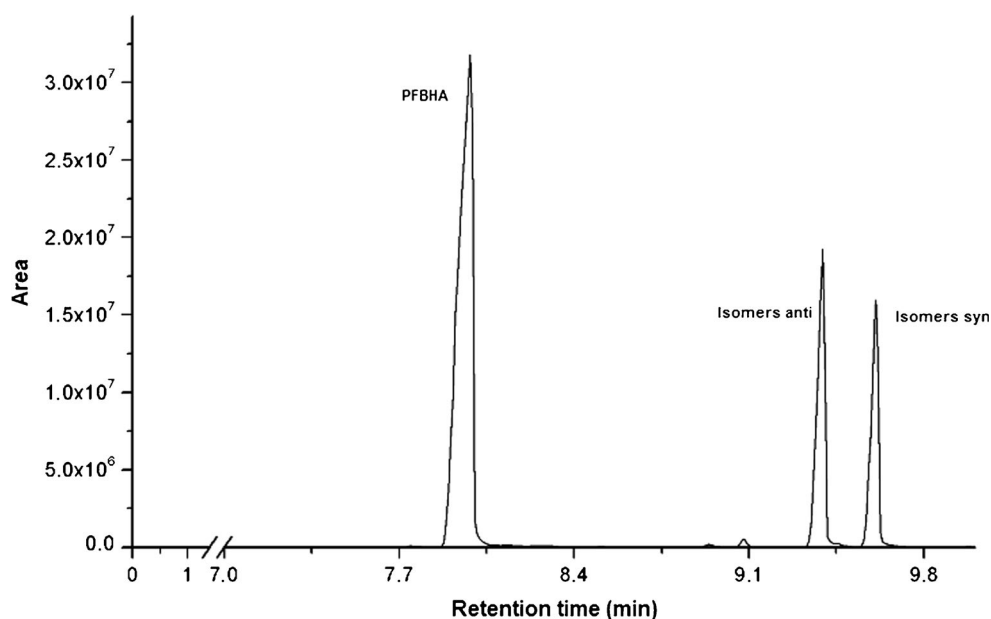
**Fig. 2** Cold fiber SPME device for breath sampling: 1—disposable cardboard mouthpiece; 2—teflon tube; 3—cooper tube containing liquid nitrogen; and 4—SPME holder



occupational environment, type of activity, location, and availability of administrators to cooperate. The investigation included places that used hot oil in their daily work: six pastry shops, one churros stand, and one restaurant; one closed room exposed to cigarette smoke; and two parking lots with constant flow car.

For each environmental sample, the cold fiber was exposed during 15 min in the breathing zone of the worker. After this exposure, the fiber was removed, packaged in aluminum foil, and conditioned at  $3 \pm 2$  °C until analysis. The maximum interval between collection and analysis did not exceed 2 h to avoid analyte volatilization.

**Fig. 3** Mass chromatogram of standard gaseous acrolein at  $136.94 \mu\text{g m}^{-3}$  analyzed by GC/MS selecting the ions  $m/z = 181$ , 250, and 432



**Table 1** Comparison of main analytical parameters obtained in this study with studies described in literature

Reference	Matrix	Derivatizing agent	Instrument	$R^2$	LOD	LOQ	Precision	
							Intra-assay	Intermediate
[13]	Exhaled breath condensate	DNPH	LC/APCI-MS/MS	0.995	1.0 nmol L <sup>-1</sup>	–	–	–
[14] <sup>a</sup>	Ambient air	DNPH	HPLC-UV	–	0.06 µg m <sup>-3</sup>	–	10%	–
[15]	Ambient air	PFBHA	GC/MS	0.995	0.15 µg m <sup>-3</sup>	–	6.7%	–
[18] <sup>a</sup>	Ambient air	DNPH	IT-SPME HPLC-UV	0.999	78 ng L <sup>-1</sup>	179 ng L <sup>-1</sup>	1.5%	–
[19]	Human urine	none	HS-SPME GC-ITMS	0.999	1 nmol L <sup>-1</sup>	–	5.79%	10.07%
[26]	Emission gases from charcoal combustion	DNPH	HPLC-UV	–	0.92 ng L <sup>-1</sup>	–	–	–
This study	Ambient air	PFBHA	CF-SPME GC/MS	0.997	2.88 µg m <sup>-3</sup>	5.02 µg m <sup>-3</sup>	6.67%	9.00%
This study	Exhaled air			0.998	2.40 µg m <sup>-3</sup>	3.79 µg m <sup>-3</sup>		

<sup>a</sup> (Acrolein + acetone)

The procedure used for exhaled air sampling of exposed individuals was the same adopted in previous work [20, 23]. However, in this study the fiber was cooled as shown in Fig. 2. Immediately after collection, the fiber was also stored at 3 ± 2 °C until GC/MS analysis.

### Statistical analysis and validation parameters

The Jackknife was used to verify presence of outliers, normality of the residuals by Ryan-Joiner test, independence of the residuals by Durbin-Watson test, homocedasticity of the residuals by Brown-Forsythe test, and regression significance and deviation from linearity by ANOVA test. All tests were performed using the Minitab 16 software from Minitab Inc (State College, PA, USA). The Origin 8.0 software from OriginLab Corp (Northampton, Northants, UK) was used to construct the graphs.

The parameters of merit linearity, intra and inter-assay precision, detection limit, and quantification limit were analyzed according EURACHEM guidelines [24].

The analytical curves for determination of acrolein in ambient and exhaled air were constructed with six concentration levels, with three repetitions for each level. The concentrations used were 59.21, 212.29, 283.40, 588.20, 1001.01, and 1498.86 µg m<sup>-3</sup>. To assess the curve linearity, some statistical tests were applied: presence of outliers (Standardized Jackknife), normality of the residuals (Ryan-Joiner test), independence of the residuals (Durbin-Watson test), homoscedasticity of the residuals (Brown-Forsythe test), regression significance and deviation from linearity (ANOVA) [25].

### Study protocol and volunteers

A protocol approved by the Ethics Committee of Universidade Federal de Minas Gerais, Brazil, was used for collection of exhaled air samples from individuals exposed to cigarette smoke. All participants signed a consent form where they agreed to participate in an informational work. Volunteers were active smokers, 13 men and 17 women with age between 20 and 55 years old. Indoor environmental sampling was realized with each volunteer smoking one cigarette indoor. After smoking, the exhaled air was collected according to the procedure described early.

### Results and discussion

Acrolein derivatization with PFBHA produces two oxime isomers (sin and anti) that are completely separated as shown in the chromatogram of Fig. 3. Nevertheless, the two isomers areas were measured as one analyzing the  $m/z$  fragments 181, 250, and 432.

The results of linearity study demonstrated that the residuals presented a normal distribution, were independent, and were heteroscedastic. Due to the heteroscedasticity responses, the analytical curve was constructed by the weighted least squares method (WLSM). The ANOVA test showed that the regression is significant and there is no deviation from linearity; therefore, the linear regression could be used for quantification of acrolein-PFBHA. The coefficient of determination ( $R^2$ ) for environmental analysis and exhaled air were 0.997 and 0.998, respectively.



Ten repetitions at concentration levels of 59.21, 588.20, and 1001.01  $\mu\text{g m}^{-3}$  were performed on the same day to evaluate intra-assay precision (repeatability). The results for ambient and exhaled air showed relative standard deviation (RDS) ranged from 6.00 to 8.00%, with an average of 6.67%. The intermediate precision was evaluated through five replicate analyzes of three concentration levels on three consecutive days. The RDS values obtained to intermediate precision study were within the range of 8.00 to 10.00%, with an average of 9.00%.

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated according to the recommendations of the EURACHEM Guide analyzing 10 blank samples. The acrolein permeation tube was removed from the permeation chamber, allowing passage of the diluent airflow for 24 h before performing the extractions. The limits obtained were LOD of 2.88  $\mu\text{g m}^{-3}$  and LOQ of 5.02  $\mu\text{g m}^{-3}$  for determination of acrolein in ambient air. For quantification of acrolein in exhaled air, LOD and LOQ were 2.40 and 3.79  $\mu\text{g m}^{-3}$ , respectively. These merit parameters are adequate to acrolein analysis in environmental and exhaled air samples. For the analysis of ambient air, the analytical performance of the developed method was similar to other related studies [14, 15, 26]. Table 1 shows different methods for acrolein analysis, the merit parameters for these methods were not completely investigated compared to the present study. Pang et al. [15] proposed an HPLC-UV method of high sensitivity collecting ambient air on a sampling tube filled with 100 mg Tenax TA. Villanueva et al. [14] also show a method with good sensitivity using HS-SPME to sampling ambient air, however, in this method acrolein coelute with acetone. The literature presents some alternative methods to determine acrolein; however, there are few works to acrolein analysis of exhaled air [27, 28], none of them has used exhaled air as biomonitoring method to assess acrolein exposition.

Application of CF-SPME method to real samples was carried out through the analysis of samples collected in ambient and exhaled air of exposed volunteer. The results showed (Table 2) that acrolein concentrations in ambient air ranged from 3.00 to 331.35  $\mu\text{g m}^{-3}$  with a median of 59.04  $\mu\text{g m}^{-3}$ . Considering international legislation regarding occupational exposure to acrolein, the concentrations found in this study are lower than NIOSH STEL exposure limit of 800  $\mu\text{g m}^{-3}$  for 15 min of exposure [22]. The concentrations found in the churros stand and in the restaurant were 26.77 and 54.03  $\mu\text{g m}^{-3}$ , respectively. The sampling performed in two closed parking lots with constant car flow showed concentrations of 6.69 and 62.92  $\mu\text{g m}^{-3}$ . On the other side, pastry shops presented concentration median of 106.07  $\mu\text{g m}^{-3}$  in the range of 7.62 to 278.23  $\mu\text{g m}^{-3}$ . It was observed that all pastry shops as well as the churros stand and the restaurant studied used soybean oil to cook. A previous study [2] showed that soybean oil present higher values of acrolein than other

**Table 2** Acrolein concentrations ( $\mu\text{g m}^{-3}$ ) in exhaled and ambient air

Location	Samples	Acrolein concentrations ( $\mu\text{g m}^{-3}$ )		
		Exhaled air	Ambient air	
Indoor air samples contaminated by cigarette smoke	1	9.71	28.62	
	2	11.67	33.57	
	3	4.25	37.46	
	4	4.20	59.44	
	5	6.67	35.52	
	6	4.56	40.33	
	7	4.83	41.41	
	8	6.56	45.56	
	9	8.27	59.85	
	10	12.32	95.48	
	11	6.17	43.88	
	12	114.58	321.32	
	13	95.86	267.66	
	14	87.36	272.61	
	15	65.52	136.92	
	16	17.59	58.64	
	17	98.77	172.46	
	18	84.39	134.55	
	19	27.51	66.06	
	20	32.57	99.35	
	21	3.86	16.85	
	22	3.84	27.86	
	23	8.43	54.41	
	Pastry shops	24	nd <sup>a</sup>	26.67
		25	nd	266.37
		26	nd	7.32
		27	nd	278.23
	Churros stand	28	nd	218.94
		29	nd	106.07
Restaurant	30	nd	26.77	
Closed parking	31	nd	54.03	
	32	nd	6.69	
	33	nd	62.92	

<sup>a</sup> Not analyzed

kinds of oil. Besides, this study showed also that reused oil presented higher concentrations of acrolein. Since it is known that pastry shops reuse oils frequently, this reuse can explain the higher values presented in pastry shops. Considering the great source of acrolein exposure from smoking of tobacco products, the developed CF-SPME-GC/MS method was also used to assess acrolein exposure from tobacco smokers. Thirty determinations of acrolein in exhaled air and in tobacco

smoking environment were realized, the results showed levels ranging from 17.98 to 181.89  $\mu\text{g m}^{-3}$  with a median of 42.93  $\mu\text{g m}^{-3}$  for exhaled air and ranging from 22.35 to 379.35  $\mu\text{g m}^{-3}$  with a median of 91.49  $\mu\text{g m}^{-3}$  for indoor air. Since people were smoking in a closed room, indoor sampling represent acute exposition; furthermore, the acrolein levels for this experiment were much higher than the median of 1  $\mu\text{g m}^{-3}$  described by Logue et al. as representative indoor air concentration of acrolein [29].

Ryan-Joiner test of acrolein concentrations in ambient and exhaled air showed a significant deviation from normality. Therefore these variables were natural log transformed to obtain approximate normal distribution. Natural log concentrations of acrolein-PFBHA in ambient air and exhaled air (Fig. 4) showed a strong tendency to linearity with a Pearson correlation coefficient of 0.901 ( $\beta = 0.590$ ,  $p < 0.0001$ ). This good correlation suggests the use of exhaled acrolein to assess acrolein environmental exposure. Recently, analysis of exhaled air has been successfully used for diagnosis and monitoring of various diseases to be a non-invasive, painless, and reflects the endogenous metabolism of the human body [30].

## Conclusion

This study proposes a new sampling method using CF-SPME with derivatization in fiber for acrolein analysis in exhaled air and ambient air by GC/MS. Standard acrolein generated by permeation tubes used to construct calibration curves allowed a better simulation of ambient air and exhaled air. This method

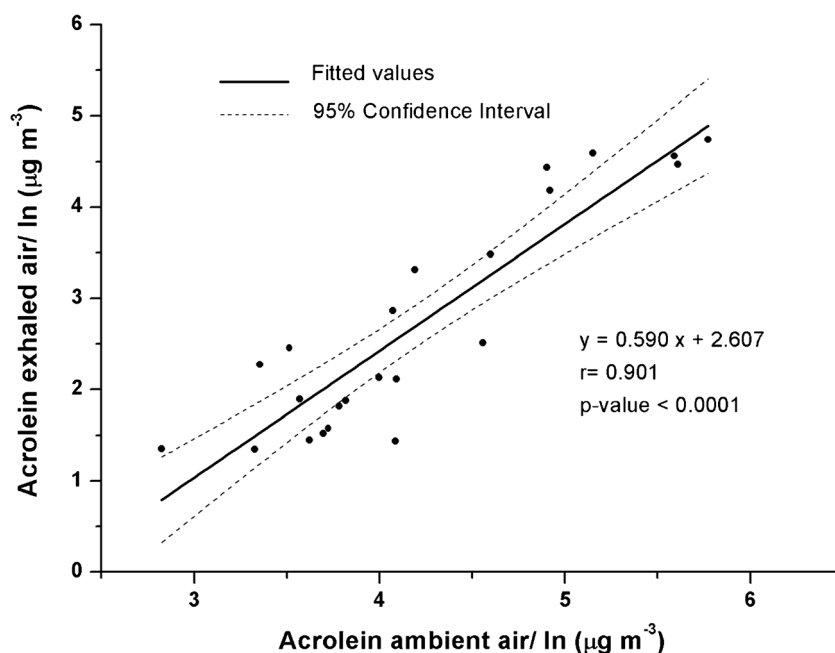
is simple and fast using a one-step sample preparation procedure; it does not consume solvents, in addition to presenting potential for portability. The validated method showed good linearity, limit of detection, limit of quantification, and adequate precision to analyze acrolein in different environments. The application to the analysis of indoor environment using hot oil showed a high range of acrolein concentration, some samples presented values higher than the level required by current legislation warning for the health of exposed people. The analysis of smokers' acrolein exposition shows that indoor acrolein concentration during smoking activities is relevant. The strong correlation between environmental air and breath analysis allows proposing acrolein analysis in exhaled air as a good technique to assess biological monitoring of acrolein exposition.

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**Compliance with ethical standards** All procedures followed were in accordance with the ethical standards of the responsible committee on human experimentation (Universidade Federal de Minas Gerais-Comitê de Ética) and with the Helsinki Declaration of 1975, as revised in 2008. Informed consent was obtained from all volunteers for being included in the study.

**Conflict of interest** The authors declare that they have no conflict of interest.

**Fig. 4** Correlation between the Ln concentration of acrolein in exhaled air and in indoor air of tobacco smoking



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