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Original Paper

Determination of carbonyl compounds in the atmosphere of charcoal plants by HPLC and UV detection

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A chromatographic quantification method with two different mobile phases (elution conditions 1 and 2) was developed to determine carbonyl compounds (CCs) in air samples collected from charcoal production workplaces, using C18 cartridges coated with 2,4-dinitrophenylhydrazine (DNPHi). Several 2,4-dinitrophenylhydrazones (DNPHo) were separated and quantified using an HPLC system and UV detection. In 16 min, elution condition 1 successfully separated and quantified the DNPHo of 14 CC including acetaldehyde, acrolein, formaldehyde, and furfural, and estimated the sum of C4 isomers, butanal–isobutanal–butanone. This elution condition was able to resolve the pairs acrolein/furfural and propanone/propanal, which have been cited in the literature as difficult mixtures to be separated. The elution condition 2 allowed separation and quantification, in less than 30 min, of 13 out of the 17 CC listed above. This elution condition was also able to separate propanone from propanal and butanone from the other components of the C4 mixture. When the two mobile phases were used together, they allowed confirmation of the presence of the DNPHo in the real samples. Thus, both elution conditions have been shown to be appropriate to determine CC, in personal and stationary samples, collected in charcoal production plants.

Keywords: Carbonyl compounds / Charcoal production / Formaldehyde / HPLC / Industrial hygiene

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1 Introduction

Carbonyl compounds (CCs) are ubiquitous in the environment, present in the gaseous, liquid, and particulate phases of the atmosphere; ocean or soils; and also in foods and beverages [1]. Wood combustion is one of the anthropogenic sources of direct CC emission into the atmosphere, generating, among others, formaldehyde, and acetaldehyde. In Brazil, the main source of CC pollution in urban areas is ethanol-fueled vehicles [2–5]. CCs have been targeted in atmospheric pollution and health-related studies due to their corrosive, irritant, and carcinogenic effects (<http://www.cdc.gov/niosh/npotocca.html>), and because they are precursors of free radicals, ozone,

peroxyalkyl nitrates, peroxyalkylbenzylates, and organic acids [6–11].

Charcoal, which is produced by burning wood in an oxygen-poor environment, has long been used in pig iron and steel production processes. In Brazil, charcoal is produced in brick kilns that are usually devoid of any system for controlling or eliminating the emission of smoke into the atmosphere. Wood smoke may contain numerous substances besides CC including benzene, naphthalene, and heavier polycyclic aromatic hydrocarbons in gaseous, liquid or particulate phases. The resulting atmospheric contamination may also affect the health of charcoal plant workers and that of the population in the proximity of charcoal plants (http://www.mct.gov.br/upd_blob/0008/8733.pdf) [12–14].

Several authors have presented comprehensive reviews on analytical methods to determine CC in the atmosphere [15, 16]. Most procedures involve sampling CC in bonded silica C18 cartridges coated with 2,4-dinitrophenylhydrazine (DNPHi) and quantifying them using HPLC coupled to several different detection systems. UV–Vis detection at a wavelength of around

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Abbreviations: CC, carbonyl compound; DNPHi, 2,4-dinitrophenylhydrazine; DNPHo, 2,4-dinitrophenylhydrazone

360 nm is one of the most commonly used techniques. However, these methods have been applied exclusively in air pollution studies of urban areas or indoor environments, where CC concentrations are relatively low [7, 9, 17–26], but have not been utilized to quantify CC in workplaces such as charcoal plants.

This article presents an analytical method for the quantification of formaldehyde, acetaldehyde, furfural, acrolein, propanone, propanal, mixtures of C4 isomers such as isobutanal-butanal-butanone, cyclopentanone, benzaldehyde, 2-pentenal, cyclohexanone, hexanal, 2-hexenal, 2-ethylhexanal, and octanal in the atmosphere, in stationary samples or personal samples, collected directly from workplace at charcoal plants, using C18-bonded silica cartridges coated with acidic DNPHi solution. The 2,4-dinitrophenylhydrazones (DNPHo) of CCs were eluted with ACN and quantified by HPLC with UV detector. This method was developed to quantify atmospheric CC in field samples from charcoal plants for industrial hygiene applications. For this reason, the sampling, and analytical conditions reported and discussed here – chromatographic parameters, LOD and LOQ, DNPHi solution concentration, sampling time and flow rate – were optimized for application in charcoal processing environment.

2 Experimental

2.1 Reagents and solutions

All the solvents were of HPLC grade and the distilled water was treated to remove organic compounds in an E-pure, model D11911 (Barnstead, Dubuque, USA) purification system. The CCs, sulfuric acid, and phosphoric acid were of PA grade (Merck, Germany). Two concentration levels of the acidic solution of DNPHi (Fluka, Switzerland), 0.05 and 0.2% m/v were prepared. Briefly, the DNPHi solutions were prepared by weighing 0.1 or 0.4 g of the pure solid and dissolving in 120 mL of ACN, 78 mL of ultrapure grade water and 2 mL of concentrated phosphoric acid. The solution was then checked for purity by extracting with 2 mL of CCl₄ and analyzing by HPLC. The DNPHi solution was stored in an amber glass bottle and kept under refrigeration (4°C). The DNPHo were synthesized by reaction of DNPHi with each CC. In an Erlenmeyer flask of 25 mL, 0.8 g of the DNPHi was dissolved by the slow addition of concentrated sulfuric acid (4 mL), followed by the slow addition of ultrapure grade water (6 mL) and stirring, up to its complete dissolution. Then, 20 mL of ethanol was added slowly under stirring. To this solution, ethanolic solutions of each CC were added individually and let to rest for 30 min at ambient temperature, followed by filtration. The filtered DNPHo were dried and put into a light protected vacuum dessicator. A more detailed description of the preparation can be

found elsewhere [27, 28]. The purity was checked by HPLC. When necessary, recrystallization was done.

Stock standard solutions in ACN (~30 mg/L) were prepared for the hydrazones of formaldehyde, acetaldehyde, furfural, acrolein, propanone, propanal, isobutanal, *n*-butanal, butanone, cyclopentanone, benzaldehyde, 2-pentenal, cyclohexanone, hexanal, 2-hexenal, 2-ethylhexanal, and octanal. The standard solutions for calibration curves were prepared by diluting stock solutions.

2.2 Cartridge preparation

Sep-Pak®-bonded C18 cartridges (360 mg, Waters, Milford, MA, USA) were coated with 0.05 and 0.2% m/v acidic DNPHi solutions 24 h before use to reduce the risk of laboratory contamination. The cartridges were preconditioned with 4 mL of ACN followed by 3 mL of an acid DNPHi solution (~5 mL/min). They were then dried in a gentle stream of UP grade nitrogen for 5 min. At the beginning of the nitrogen flow, two DNPHi-coated cartridges were connected in tandem to prevent contamination of sampling cartridges during their preparation [2, 7]. After the cartridges were dried and their ends capped, they were wrapped in Teflon® tape and aluminum foil and placed in hermetically closed plastic bags, which were stored in plastic containers inside a desiccator in a freezer. Cellulose filters coated with DNPHi solution were placed inside each plastic container or bag to trap any CC present in the air.

2.3 Sampling

CCs were collected from the atmosphere by pumping air into two tandemly connected cartridges using personal sampling pumps (SKC, Eighty-Four, USA; Air Check 2000 and 224-PCXR-3 models). In the collection system (shown schematically in Fig. 1), the cartridges were positioned so as to introduce air in the same direction as their coating of DNPHi solution. The second cartridge (control) served to evaluate sampling efficiency by detecting breakthroughs in the first cartridge. Before reaching the cartridges, the air samples passed through an ozone scrubber consisting of a 37 mm holder containing two cellulose filters coated with potassium iodide (5%) to prevent oxidation of DNPHi or DNPHo by ozone. After sampling, the ends of the main and control cartridges were closed with plastic caps and Teflon tape, the cartridges were wrapped individually in aluminum foil, placed in sealed plastic bags and stored in a refrigerator until their elution and analysis. Coated cartridges from the same set as the ones used for sampling were used as blanks and control to estimate background levels in the laboratory and field.

Tests were conducted initially at charcoal plants near Salvador – capital of the state of Bahia, in Brazil –

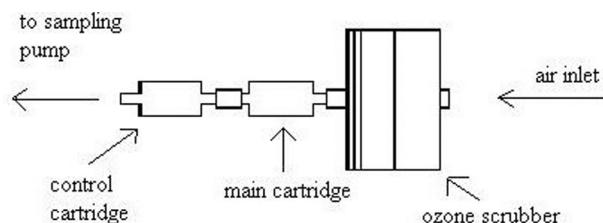


Figure 1. CC sampling system equipped with ozone scrubber.

located at 13°01'S and 38°31'W on the Atlantic coast. Stationary air samples were collected close to (~1.5 m) the carbonization kilns (emission source), with a stand telescope, holding the sampling system at the height of ca. 1.6 m. Personal air samples were collected attaching the system close to the workers' breathing zone (chest/neck region) while performing their tasks around the kilns. In this case, the optimum flow rate, to keep the pumps operating stably for at least 4 h, was 0.1 L/min, resulting in a total of ~24 L of air. With this collection system, pumps could not be operated at flow rates over 0.1 L/min. Therefore, adjustable low flow holders (SKC, Eighty-Four) were attached to them. Before each sampling, pumps with low flow holders were calibrated with a digital flowmeter (SKC, Eighty-Four; AccuFlow model). After sampling, the flow rates were measured again to check variations in collected air volume. The maximum acceptable flow rate error was 10%.

2.4 Analysis

The DNPHo compounds found in cartridges were slowly eluted with ACN (~5 mL). Eluates, when not immediately analyzed, were kept for up to 2 wk under refrigeration to ensure sample stability [7, 21, 25, 29, 30]. Aliquots of 20 μ L of each sample were injected onto a Merck Lichrospher® 100, RP 18, column ($l = 250$ mm $id = 4.6$ mm, $d_p = 5$ μ m) (~25°C) using a Rheodyne 7125 injector valve. The HPLC system (PerkinElmer, Norwalk, USA, 200 series) was equipped with a binary gradient pump and a UV-Vis detector adjusted to 365 nm.

Two different mobile phases and gradient conditions, defined as elution conditions 1 and 2, were developed to separate furfural from acrolein, propanone from propanal, and butanone from other C4 isomers. Elution condition 1 consisted of ACN/water 75:25 v/v as phase A and 100% ACN as phase B, with the following stepwise gradients: 100% A (0–6 min), 10% A (6–20 min), and 100% A (20–25 min). In elution condition 2, the methanol/ACN/water 74.5:0.5:25% by volume mixture was used as phase A and methanol 100% as phase B and the gradient was 100% A (0–12 min), 10% A (12–20 min), 10% A (20–26 min), and 100% A (26–32 min). In both elution conditions, the mobile phase flow rate was 0.8 mL/min. The

analytical precision was determined with injections of replicated samples. The quantification was conducted using an external standard, and the solution concentration was calculated by means of calibration curves.

The LOD and LOQ for both chromatographic elution conditions were calculated using the following equations:

$$\text{LOD} = \frac{3s}{A} \quad (1)$$

$$\text{LOQ} = \frac{10s}{A} \quad (2)$$

where s is the SD of the linear regression curve and A is its angular coefficient. A specific low concentration curve was constructed to determine the parameters for those limit values, for each CC in both elution conditions, following a method described elsewhere (<http://www.osha.gov/dts/sltc/methods/index.html>) [31]. However, due to the high concentrations expected to be found in the charcoal plants, calibration curves with higher concentration ranges were used for sample quantification. The recovery efficiency of the DNPHo of the collected CC was assessed by a second elution of the main cartridges of samples containing mixtures with numerous components or higher amounts of the components of interest.

3 Results and discussion

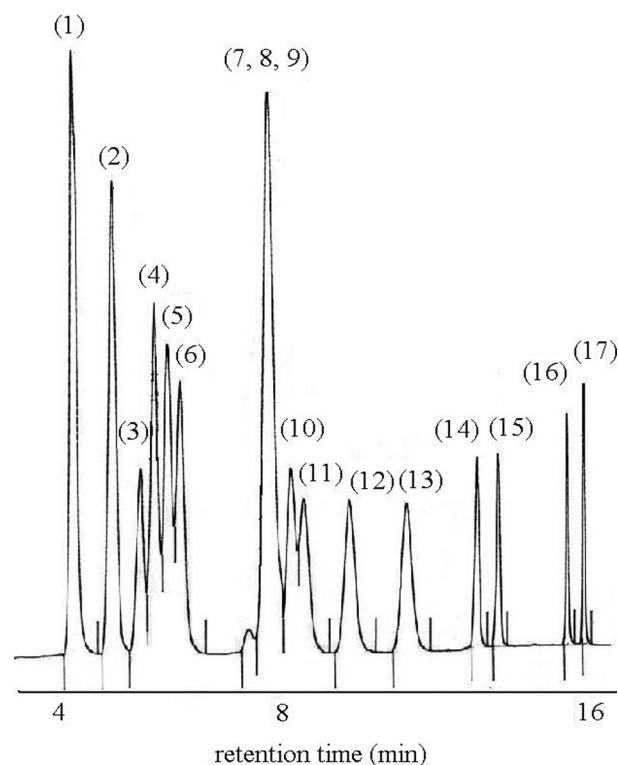
3.1 Analytical procedures

Figures 2 and 3 show chromatograms of the hydrazones of 17 CC present in the standard mixture obtained under the two elution conditions. Elution condition 1 allowed separation and quantification, in 16 min, of 14 out of 17 analyzed DNPHo. This condition was able to resolve the pairs acrolein/furfural and propanone/propanal, which have been cited in the literature as difficult mixtures to be chromatographically separated [9, 15, 17]. Table 1 presents the average retention times and parameters for the calibration curve built according to elution condition 1.

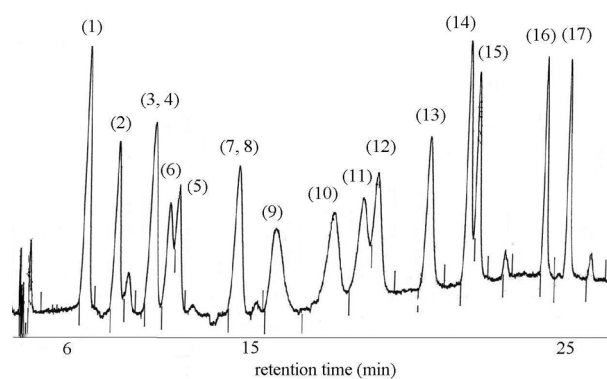
The elution condition 2, enabled the separation and quantification of the same DNPHo mixture but, unlike condition 1, it was able to separate butanone from the other two C4 isomers. It should also be noted that propanal and propanone eluted in the inverse order from that of elution condition 1. Table 2 presents the average retention times and parameters for the calibration curve constructed according to elution condition 2, with the HPLC detector operating at the same degree of sensitivity as in condition 1. The results obtained with these two elution conditions showed good correlations and linearity between compound concentrations and detector response for all the DNPHo studied here ($r = 1.00$). The

Table 1. Parameters of elution (retention time – RT) and of calibration curves for CC determined by elution condition 1 ($r = 1.00$)

	CC	RT (min)	Calibration curve parameters		
			Conc. range (ng/mL)	Slope (counts (ng/mL) ⁻¹)	Intercept (counts)
1	Formaldehyde	4.09	16.0–608.2	17.02	18.28
2	Acetaldehyde	4.75	15.7–597.4	13.72	11.86
3	Furfural	5.20	14.6–495.8	6.13	-6.05
4	Acrolein	5.46	14.8–494.4	11.54	17.38
5	Propanone	5.70	15.6–593.0	9.13	8.38
6	Propanal	5.89	13.2–500.3	9.76	14.56
7, 8, 9	Isobutanal + butanal + butanone	7.39	46.3–586.7	5.45	6.41
10	Cyclopentanone	7.83	29.3–556.5	5.34	5.91
11	Benzaldehyde	7.97	29.7–563.4	4.38	7.22
12	2-Pentenal	8.74	13.4–508.1	5.38	1.18
13	Cyclohexanone	9.73	16.2–616.6	4.34	5.47
14	2-Hexenal	11.46	14.8–562.8	4.34	0.78
15	Hexanal	12.31	15.7–597.4	4.48	2.23
16	2-Ethylhexanal	15.09	15.8–600.4	5.62	3.29
17	Octanal	15.74	14.1–537.3	7.85	0.44

**Figure 2.** Chromatogram of a standard mixture containing 17 CC (as DNPHo) determined by elution condition 1. Formaldehyde (1); acetaldehyde (2); furfural (3); acrolein (4); propanone (5); propanal (6); isobutanal + *n*-butanal + 2-butanone (7, 8, 9); cyclopentanone (10); benzaldehyde (11); 2-pentenal (12); cyclohexanone (13); 2-hexenal (14); hexanal (15); 2-ethylhexanal (16); and octanal (17).

application of the two elution conditions to CC (as DNPHo) mixtures allowed for the complete separation and independent quantification of 15 out of 17 CC (as

**Figure 3.** Chromatogram of a standard mixture containing 17 CC (as DNPHo) determined by elution condition 2. Formaldehyde (1); acetaldehyde (2); furfural + acrolein (3, 4); propanal (6); propanone (5); isobutanal + *n*-butanal (7, 8); 2-butanone (9); cyclopentanone (10); benzaldehyde (11); 2-pentenal (12); cyclohexanone (13); 2-hexenal (14); hexanal (15); 2-ethylhexanal (16); and octanal (17).

DNPHo) analyzed in this study and the confirmation of the presence/absence of these substances in real samples of charcoal plants by direct comparison with the chromatograms of the standards.

3.2 LOD and LOQ

The calculation of the LODs for CC in atmospheric samples, through air volumes of around 100 L, has been a common practice in several studies. Table 3 shows some of the results presented by several authors [7, 9, 20, 25, 29, 32]. The values illustrate the variability of the results among these studies, probably due to differences in the methods employed and in the range of environmental contamination from which the samples originated.

Table 2. Parameters of elution (retention time, RT) and of calibration curves for CC determined by elution condition 2 ($r = 1.00$)

CC	RT (min)	Calibration curve parameters			
		Conc. range (ng/mL)	Slope (counts (ng/mL) ⁻¹)	Intercept (counts)	
1	Formaldehyde	6.06	16.0–608.2	6.61	9.95
2	Acetaldehyde	7.82	31.4–597.4	4.62	-5.12
3, 4	Acrolein + furfural	9.87	29.4–1005	3.08	-33.8
6	Propanal	10.78	13.2–500.3	3.56	-3.28
5	Propanone	11.27	31.2–593.0	3.22	-4.06
7, 8	Isobutanal + butanal	14.68	30.3–1151	2.07	0.940
9	Butanone	16.79	32.0–608.4	2.10	-5.33
10	Cyclopentanone	18.52	14.6–556.5	2.44	-1.90
11	Benzaldehyde	19.37	29.7–563.4	2.65	0.34
12	2-Pentenal	19.79	26.7–508.1	3.72	-10.83
13	Cyclohexanone	21.41	16.2–616.6	3.75	-5.31
14	2-Hexenal	22.59	14.8–562.8	6.29	-11.1
15	Hexanal	22.85	15.7–597.4	5.64	-15.9
16	2-Ethylhexanal	24.89	15.8–600.4	5.40	-0.510
17	Octanal	25.59	28.3–537.3	6.45	7.82

Table 3. LODs of studied CC reported by several authors and obtained in this study, expressed as concentration in air, in ppbv, considering a volume of 100 L of air

CC	Other authors						This study	
	[7]	[9]	[20]	[25]	[29]	[32]	Elution condition 1	Elution condition 2
Acetaldehyde	1.11	0.8	0.18	1.39	–	1.00	0.02	0.21
Acrolein	0.06	0.4	–	1.49	–	–	0.04	–
Acrolein + furfural	–	–	–	–	–	–	–	0.06
Benzaldehyde	0.11	0.5	–	0.94	0.37	–	0.08	0.08
Butanal	0.12	–	0.2	0.74	0.41	–	–	–
Butanal + butanone	–	–	–	–	–	–	–	0.05
Butanone	0.13	–	–	–	0.64	–	–	0.12
Cyclohexanone	0.12	–	–	–	–	–	0.03	0.06
Cyclopentanone	–	–	–	–	–	–	0.04	0.06
2-Ethylhexanal	–	–	–	–	–	–	0.01	0.04
Formaldehyde	0.75	1	0.18	1.39	–	0.50	0.03	0.18
Furfural	–	–	–	0.77	–	–	0.03	–
Hexanal	0.26	0.5	–	–	0.21	–	0.03	0.06
2-Hexenal	–	–	–	–	–	–	0.04	0.06
Isobutanal + butanal + butanone	–	–	–	–	–	–	0.02	–
Metacrolein + butanal + butanone	–	0.6	–	–	–	–	–	–
Octanal	–	–	–	1.08	0.14	–	0.01	0.05
2-Pentenal	–	–	–	–	–	–	0.03	0.08
Propanal	0.2	0.5	–	0.5	0.15	–	0.04	0.06
Propanone	0.5	24.6	0.44	–	0.10	–	0.05	0.20

Table 3 also presents the LOD values obtained in this study, in ppbv, considering a volume of 100 L. The higher sensitivity of the method presented in both chromatographic elution conditions, is clearly visible.

Table 4 presents the LOQs obtained by these two elution conditions, expressed as CC concentration in the solutions (ng/mL) and 24 L of air samples (in ppbv), which was the sample volume employed throughout the present study. The values in ng/mL enable direct compar-

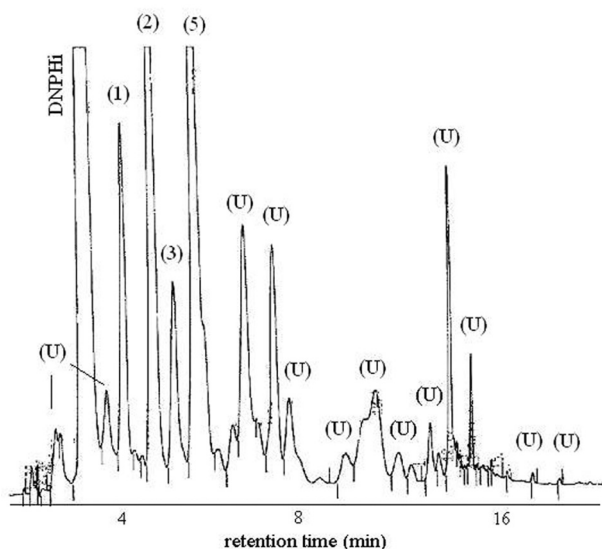
ison with the lowest concentration of the curve presented in Tables 1 and 2. The elution condition 1 had smaller LOD and LOQ than elution condition 2 for all quantified substances, thus showing higher sensitivity.

3.3 Precision

Analyses of standard solution replicates presented RSDs mostly equal to or below 5%. The highest deviations were

Table 4. LOQ of CC obtained in this study, expressed as concentration in solution, in ng/mL, and concentration in air, in ppbv, considering a volume of 24 L of air

CC	ng/mL		ppbv	
	Elution condition 1	Elution condition 2	Elution condition 1	Elution condition 2
Acetaldehyde	3.0	25.3	0.35	2.92
Acrolein	6.5	–	0.59	–
Acrolein + furfural	–	15.1	–	0.80
Benzaldehyde	21.7	22.8	1.04	1.10
Butanal + isobutanal	–	10.7	–	0.75
Butanal + isobutanal + butanone	3.5	–	0.25	–
Butanone	–	22.9	–	1.61
Cyclohexanone	8.4	15.7	0.44	0.81
Cyclopentanone	9.0	14.7	0.55	0.89
2-Ethyl hexanal	4.0	15.5	0.16	0.62
Formaldehyde	2.1	15.1	0.36	2.56
Furfural	8.3	–	0.44	–
Hexanal	9.4	78.1	0.48	0.79
2-Hexenal	9.6	15.1	0.50	0.78
Octanal	2.0	17.0	0.08	0.68
2-Pentenal	7.9	17.8	0.48	1.08
Propanal	6.4	10.0	0.56	0.88
Propanone	7.2	32.4	0.63	2.86

**Figure 4.** Chromatogram of the main cartridge of a stationary sample showing the DNPHi peak in excess obtained by elution condition 1 and the DNPHo of determined CC: formaldehyde (1); acetaldehyde (2); furfural (3); propanone (5); and unknown (U).

observed in situations where compound separation was poor or when the concentration was low, close to the LOD. Environmental samples collected in parallel generally showed a higher overall relative deviation (sampling + lab analysis) than that of standard solution tests, as has been observed in other studies [7, 29]. The overall relative deviation was determined for formaldehyde (8.8%), acetaldehyde (6.1%), propanone (18.0%), and the sum of C4 isomers (16.5%).

3.4 Field tests at charcoal plants

Exploratory field sampling conducted at two different charcoal plants showed that Sep-Pak C18-bonded silica cartridges coated with 0.05% m/v DNPHi solution were inadequate for evaluating these environments, considering the sampling parameters adopted (pump flow rate of 0.1 L/min and sampling time of ~2.5 h). In this situation, all the derivatizing reagents were consumed in the main and control cartridges, and breakthrough from 50 to 600% was observed. Similar levels of breakthrough were found in stationary samples collected for ~5 h in C18 cartridges coated with 0.2% m/v DNPHi solution. This can be explained by the fact that the stationary samples were placed in the most critical conditions, *i.e.*, close to the sources of emission (kilns) where the temperature (30–35°C) and CC concentration levels are higher. In such situations, reducing the sampling time was a strategy to reduce cartridge saturation and breakthrough. Cartridges coated with 0.2% m/v DNPHi solution used for personal sampling for up to 4 h at the same flow rate (0.1 L/min) presented no breakthrough. Also, these cartridges have proved to be suitable for stationary samples collected for up to 130 min. The chromatogram in Fig. 4 was obtained from the main cartridge of a stationary sample analyzed according to condition 1. The presence of the DNPHi peak is evidence that the reagent was not totally consumed, indicating that the sample was efficiently collected. Elution tests revealed that one elution was enough for complete recovery of the CC hydrazones.

Field tests conducted at two charcoal plants allowed for the quantification of personal samples ($n = 11$) in the following ranges: 15–139 $\mu\text{g}/\text{m}^3$ of formaldehyde; 38–

165 $\mu\text{g}/\text{m}^3$ of acetaldehyde; 39–114 $\mu\text{g}/\text{m}^3$ of furfural; 26–363 $\mu\text{g}/\text{m}^3$ of propanone; and 11–115 $\mu\text{g}/\text{m}^3$ of C4 mixture (as butanone). In stationary samples ($n = 8$), the ranges were as follows: 20–160 $\mu\text{g}/\text{m}^3$ of formaldehyde; 111–284 $\mu\text{g}/\text{m}^3$ of acetaldehyde; 70–163 $\mu\text{g}/\text{m}^3$ of furfural; 328–644 $\mu\text{g}/\text{m}^3$ of propanone; and 100–176 $\mu\text{g}/\text{m}^3$ of C4 mixture (as butanone). Acrolein, cyclopentanone, 2-pentenal, and CC > C8 were not detected in personal or stationary samples in either of the chromatographic conditions.

When using elution condition 2, unknown substances eluting at the same retention times as propanal, benzaldehyde, butanone, cyclohexanone, 2-hexenal, hexanal, 2-ethylhexanal, and octanal were observed in field samples. However, the use of the elution condition 1 also developed in this work enabled us to conclude that these substances were not the CC previously supposed, since they did not reproduce the same retention times of those compounds for this second condition, thus reinforcing the importance of the chromatographic methods developed in our study. Figure 4 also shows the presence of several peaks considered unknown after the sample was analyzed under both chromatographic conditions. These substances could not be identified and quantified due to the unavailability of standards. Further studies involving HPLC-MS are in progress in an attempt to identify these compounds.

4 Conclusions

In the present study, a conventional method for the determination of vapor CC in air, which involved active CC sampling in cartridges impregnated with acid DNPH solution, followed by the extraction of DNPH derivatives, and quantification by HPLC-UV, was optimized to enable the determination of various CC present in personal and area samples collected in charcoal plant atmospheres, by subjecting the same sample to two chromatographic elution conditions. This approach enabled the complete separation and independent quantification of 15 out of 17 CC (as DNPH) analyzed in this study. The advantage of elution condition 1 was the complete separation of the acrolein/furfural and propanone/propanal pairs, which have been cited in the literature as difficult mixtures to be chromatographically separated, as well as the rapid separation and quantification (~ 7 min) of formaldehyde, acetaldehyde, acrolein, furfural, propanone, propanal, and C4 isomers. On the other hand, the benefit of the elution condition 2 was the separation of the butanone from other components of the C4 isomer mixture. Additionally, when the two protocols were used together, they enabled us to discard substances previously supposed to be present in the samples. When using elution condition 2, unknown substances eluting at the

same retention times as propanal, benzaldehyde, butanone, cyclohexanone, 2-hexenal, hexanal, 2-ethylhexanal, and octanal were observed in field samples. However, the use of the elution condition 1 also developed in this work enabled us to conclude that these substances were not the CC previously supposed, since they did not reproduce the same retention times of those compounds for this second condition.

Cartridges containing 360 mg of bonded C18, such as Sep-Pak, coated with 0.2% m/v of DNPH solution, were efficient in collecting CC in the workplace atmosphere of charcoal plants, when the sampling duration did not exceed 240 min for personal sampling and 130 min for area sampling, with an airflow of around 0.1 L/min.

The method allowed for the quantification of personal samples in the following ranges: 15–139 $\mu\text{g}/\text{m}^3$ of formaldehyde; 38–165 $\mu\text{g}/\text{m}^3$ of acetaldehyde; 39–114 $\mu\text{g}/\text{m}^3$ of furfural; 26–363 $\mu\text{g}/\text{m}^3$ of propanone; and 11–115 $\mu\text{g}/\text{m}^3$ of C4 mixture (as butanone). In stationary samples, the ranges were the following: 20–160 $\mu\text{g}/\text{m}^3$ of formaldehyde; 111–284 $\mu\text{g}/\text{m}^3$ of acetaldehyde; 70–163 $\mu\text{g}/\text{m}^3$ of furfural; 328–644 $\mu\text{g}/\text{m}^3$ of propanone; and 100–176 $\mu\text{g}/\text{m}^3$ of C4 mixture (as butanone).

Acrolein, cyclopentanone, 2-pentenal, and CC > C8 were not detected in personal or stationary samples in either of the chromatographic conditions. Several unknown peaks were detected in the field samples, indicating the need for further investigation. The identification of these compounds will allow for a more reliable evaluation of workplace contamination and workers' exposure to the CC of charcoal plant wood smoke.

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