Aldehydes, Acetone, Formic and Acetic Acids in Indoor Air of an Office Building

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One of the objectives of our study was to evaluate and compare the levels of aldehydes and ketones in indoor air in offices. Also, we wanted to determine and discussed indoor concentrations of formic and acetic acids in the same offices. As so, a total number of seventeen carbonyls were scanned in indoor air samplers. Aldehydes and ketones were quantified using a DNPH-derivatization method followed by liquid chromatography coupled to UV detection. For the determinations of formic and acetic acids, a fast ion chromatography analytical method was developed. Results obtain showed the presence of the interested compounds in all the sampling offices and also possible sources.

Keywords: indoor air, carbonyls, carboxylic acids, aldehydes, formaldehyde

In our daily lives we are confronting more and more with indoor air pollution due to an increasing amount of time spent indoor. Studies on indoor air revealed the presence of numerous pollutants including aldehydes, with formaldehyde being the most interested for human health, and other indoor organic pollutants.

Aldehydes, ketones and formic and acetic acids are commonly named carbonyls. Indoor air studies on carbonyls started to be conducted in'90, and it is still in the area of interest in terms of air pollution nowadays. Many of these studies were realized in work environments, as factories and process utilities, and as timed passed moved on in other indoor environments where they weren't found currently such as offices [1-3].

A lot of focus was done on aldehydes effects on human health, especially after formaldehyde and acetaldehyde were listed as probable human carcinogen by US EPA [4, 5] and human carcinogen by IARC [6]. Formic acid was identified as intermediate from the photodegradation of formaldehyde, degradation rate depending on the humidity levels [7]. Long term exposure to formic and acetic acids can cause allergies [8, 9].

The main source of carbonyls indoor is represented by furniture and building materials emissions. From furniture, carbonyls emission was found in particleboard, plywood and fiberboard furniture, due to formaldehyde resin glues used [10, 11]. In offices, to these emissions are added concentrations from electronic equipment like the ones used for copying documents [12]. Carbonyls are highly reactive and also can be formed as secondary pollutant from the reaction of primary pollutants.

In this study we investigated the indoor concentrations of aldehydes, acetone, formic and acetic acids in a number of different offices from a new office building. In order to establish if there are indoor sources, concentrations of outdoor air were investigated and compared to indoor ones. In recent years well establish methods went alongside innovative methods [13] for determining these pollutants; as so, for aldehydes and ketones we implemented an EPA method and for formic and acetic acids we develop a new method.

Experimental part

Sampling was done in a new office building, constructed four years ago (2011), located on a residential area in the outskirts of Bucharest (Romania). The offices were chosen to have different occupancy rate, to be on different floors, and all of them having computers and copy machines; as seen in table 1. Sampling campaign was done from 5th to

Table 1

CARACTERISTISC OF THE OFFICES USED AS SAMPLING POINTS

Office (sample name)	*Activities/ equipments/ furniture*	*Office volume (m³)*	*Number of habitants*	*Occupancy rate (m³/habitant)*
A1	Office activities/ 6 computers, copy machines/ old furniture	91.5	6	15.25
A2	Office activities/ 1 computers, copy machines/ new furniture	66.88	1	66.88
A3	Office activities/ 2 computers, copy machines/ old furniture	57.6	2	28.8
A4	Office activities/ 10 computers, copy machines/ new furniture	211.52	10	21.15

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11th of May 2015. All the sampling took place after work program, continued by night, until 8 AM next morning.

For the collection of aldehydes and ketones in indoor and outdoor air, ORBO™-555, 6 mm O.D. x 110 mm length, dual-layer silica gel coated with DNPH glass sorbent tubes from Sigma-Aldrich was purchase. Ozone interferences were eliminated by a potassium iodide (KI) ozone scrubber set upstream the sampling tube. Formic acid was collected on ORBO™ 52 small activated silica gel (20/40), O.D. × L 6 mm × 75 mm, dual-layer (150/75 mg) glass sorbent tubes also from Sigma-Aldrich. Sampling flow was set at 1.0 L* min^{-1} for aldehydes and ketones and 0.5 to 1 L* min^{-1} for formic acid. Silica gel DNPH sampling tubes were extracted in 5 mL volumetric flask with acetonitrile and analyzed within 7 days. Silica gel sampling tubes for formic acid were extracted in 10 mL volumetric flask in water with conductivity lower than 1μS. Calibration standard TO11/IP 6A Aldehyde/Ketone-DNPH Mix certified reference material, with 15 μg/mL concentration of aldehydes and ketones was purchased from Sigma-Aldrich. For the determination of formic acid and acetic acid, as formate and acetate, standars of 1000 μg/mL for each in water were purchased from LGC Standards.

Table 2

HPLC GRADIENT FOR THE DETERMINATION OF ALDEHYDES AND KETONES

Time (min)	*Acetonitrile (%)*	*Water (%)*
0.0	60	40
30.0	75	25
50.0	100	0
55.0	100	0
55.1	60	40
70.0	60	40

A high performance liquid chromatograph model Agilent 1200, coupled with a UV detector was used for the determination of aldehydes and ketones. Analytical conditions included two Acclaim Carbonyl C18 columns (250 mm * 4.6 mm, 5 μm,) coupled in series, a diode array detector (DAD) set at 365 nm wavelength, 2 mL/min flow rate, 25 μL injection volume, 25°C column temperature and a gradient mobile phase of acetonitrile / water as seen in table 2.

An ion chromatography system model Dionex ICS-5000+ Integrated Reagent Free, equipped with a conductivity detector and an Anion Self-Regenerating Suppressor (Dionex AERS 500 2mm) was used for formic and acetic acids quantifications. Separation was done on an IC Dionex IonPac AS 18 column with guard. The analytical conditions included an isocratic elution, with 10mM KOH eluent for 20 min, column temperature of 20°C and 5 μL injection volume.

All the seventeen carbonyls determined in this study are described in table 3; their retention time determined in the methods developed in this study also can be seen in the same table.

Results and discussions

Indoor temperature and humidity were monitored using a room hygro-thermometer (Testo 608-H1 model), at the beginning, in between and at the end of the sampling period for each office. Distribution of temperature and humidity over the sampling period can be seen in table 4.

Table 3

COMPOUNDS OF INTEREST AND THEIR RETENTION TIME

Formaldehyde	CH_2O	50-00-0	13.2
Acetaldehyde	C_2H_4O	75-07-0	15.9
Acetone	C_3H_6O	67-64-1	19.0
Acrolein	C_3H_4O	107-02-8	19.3
Propionaldehyde	C_3H_6O	123-38-6	20.7
Crotonaldehyde	C_4H_6O	123-73-9	23.9
Butyraldehyde	C_4H_8O	123-72-8	25.8
Benzaldehyde	C_7H_6O	100-52-7	28.9
Isovaleraldehyde	$C_5H_{10}O$	590-86-3	30.6
Valeraldehyde	$C_5H_{10}O$	110-62-3	31.9
o-Tolualdehyde	$CH_3C_6H_4CHO$	529-20-4	34.2
m-Tolualdehyde	$CH_3C_6H_4CHO$	620-23-5	34.8
p-Tolualdehyde	$CH_3C_6H_4CHO$	104-87-0	35.2
Hexaldehyde	$C_6H_{12}O$	66-25-1	38.4
2,5-Dimethylbenzaldehyde	$(CH_3)_2C_6H_3CHO$	5779-94-2	39.8
Formic acid	CH_2O_2	64-18-6	4.98
Acetic acid	$C_2H_4O_2$	64-19-7	4.36

Table 4

TEMPERATURE AND HUMIDITY CONDITIONS OF THE SAMPLING POINTS

	Temperature (°C)			*Humidity (%)*		
	Mean	Min	Max	Mean	Min	Max
A1	27.1	24.2	28.1	46	42	48
A2	24.5	23.2	26.0	33	27	39
A3	25.2	27.4	22.3	41	46	39
A4	24.5	22.2	25.6	30	29	33

Table 5
CONCENTRATIONS OF THE INTERESTED CARBONYLS AND THE INDOOR/OUTDOOR RATIO

	A1		*A2*		*A3*		*A4*		*Outdoor*
	(μg/m³)	*I/O*	*(μg/m³)*	*I/O*	*(μg/m³)*	*I/O*	*(μg/m³)*	*I/O*	*(μg/m³)*
Formaldehyde	38.30	>1	42.00	>1	31.48	>1	41.53	>1	0.61
Acetaldehyde	14.12	>1	9.94	>1	4.97	>1	24.09	>1	0.53
Acetone+Acrolein	10.89	>1	4.94	>1	3.49	>1	11.14	>1	0.95
Propionaldehyde	2.49	>1	4.46	>1	0.77	>1	3.31	>1	0.05
Crotonaldehyde	0.05	>1	0.13	>1	0.03	>1	0.15	>1	0.01
Butyraldehyde	1.68	>1	1.76	>1	1.11	>1	2.10	>1	0.37
Benzaldehyde	2.99	>1	1.25	>1	3.27	>1	1.44	>1	0.05
Isovaleraldehyde	0.44	>1	0.07	>1	0.22	>1	0.53	>1	0.02
Valeraldehyde	2.94	>1	3.92	>1	1.82	>1	3.37	>1	0.02
o-Tolualdehyde	0.12	>1	0.49	>1	0.37	>1	0.43	>1	0.08
m-Tolualdehyde	0.10	>1	0.05	>1	0.04	>1	0.13	>1	0.02
p-Tolualdehyde	0.63	>1	0.07	>1	0.22	>1	0.34	>1	0.07
Hexaldehyde	12.76	>1	15.01	>1	6.91	>1	9.98	>1	0.06
2,5-Dimethylbenzaldehyde	0.08	>1	0.07	>1	0.04	>1	0.05	>1	0.02
Formic acid	3.25	>1	2.37	>1	5.97	>1	4.78	>1	0.75
Acetic acid	8.45	>1	3.23	>1	15.47	>1	25.31	>1	2.22

I/O-Indoor/Outdoor Ratio

Concentration of all the carbonyls were quantified by external standard calibration, the calibration curves covered the range of interest and showed good linearity - $r^2 > 0.999$ (examples: $r^2=0.9990$ and $y=0.8255x-3.2277$ for formaldehyde; $r^2=0.9999$ and $y=0.5312x-0.5874$ for acetaldehyde; $r^2=0.9993$ and $y=0.5266x-4.5958$ for crotonaldehyde).

As discussed in literature [14], the traditional DNPH method is unsuitable for complete separation of acroleine from acetone. Concentrations of the mentioned aldehydes will be referred as acroleine+acetone in this study.

The results obtained regarding the pollutants concentrations can be found in table 5. According to the results, all the interested compounds were found in every air sample taken from offices. Based on the concentrations obtained the aldehydes were divided into two groups.

The highest concentrations were obtained for formaldehyde, acetaldehyde, acrolein+acetone and hexaldehyde. The values obtained for formaldehyde were similar in all the offices, with a mean of 38.33 μg/m³. Regarding acetaldehyde, office A4, characterized by the lowest occupancy rate from all the sampling points, with the highest number of habitants, had, by far, the highest concentrations, with almost two times higher than the next value obtained. The pattern for acrolein+acetone showed two offices with similar values, followed by the other two who had concentrations two times smaller the ones mentioned earlier. The other aldehydes had quantifiable concentrations that were significant lower than the concentrations of first aldehydes presented. Regarding formic and acetic acids concentrations, the lowest concentration found for the two acids were in office A2, characterized as a small office, with a high occupancy rate an only one person working there.

Based on the results presented in table 5, the Indoor/Outdoor Ratio for each office is greater than 1, suggesting the presence of indoor sources for aldehydes, acetone, formic and acetic acids.

The most common aldehydes studied in air samplers are formaldehyde and acetaldehyde. Table 6 presents the results obtain in literature in indoor offices and in this study for the two aldehydes. Comparing our results with other studies, the concentrations obtain in this study are in the same range, being situated near the mean of the all intervals showed in table 6.

Concentration of aldehydes increases indoor and outdoor when temperature is rising [22]. Also, the efficiency of formaldehyde converting to formic acid decreases with increasing humidity levels [7]. In order to determine if there are any correlations between humidity and temperature with the concentrations of formaldehyde and/or formic acid, as suggested in literature [7, 22], the data obtained were statistically analyzed. The scatter plots of humidity and then temperature against concentration of formaldehyde and concentration of formic acid didn't show a visible correlation. This can be attributed to the fact that humidity and temperature in offices do not vary so much in order to be able to determine if the concentration of the targeted pollutants can be affected by humidity or temperature.

Using the Pearson Correlation, it was establish that it is a low to medium correlation between the interested

Table 6
CONCENTRATIONS OF FORMALDEHYDE AND ACETALDEHYDE OBTAINED IN INDOOR AIR OFFICES

Formaldehyde	*Acetaldehyde*		
Concentrations (μg/m³)		*Location*	*References*
23	7	France	R. Meininghaus et al. (2003) [15]
35.5	17.1	Bangkok (Thailand)	M. Ongwandee (2009) [16]
12.2–99.7	-	Rio de Janeiro (Brazil)	Brickus et al. (2003) [17]
22.6	8.5	Beijing(China)	C. Jiang and P. Zhang (2012)[14]
22.5-161.5	18.3- 91.2	Brazil	Calvacante et al. (2005) [18]
4.64–18.37	-	Brazil	Calvacante et al. (2006) [19]
14.4–56	-	Lublin (Poland)	M. R. Dudzińska et al. (2009) [20]
11-97	5-47	Mexico City and Xalapa (Mexico)	A. Baez et al. (2005) [21]
31.42-42.00	4.97-24.09	Bucharest (Romania)	This work

pollutants and the occupancy rate of each office. Good correlation was showed analyzing the concentrations of formaldehyde with the concentrations of formic acid. The results found in this paper showed that the concentration of formic acid increases when the concentration of formaldehyde decreases, suggesting that a part of formaldehyde is photodegradeted to formic acid.

Conclusions

All the seventeen carbonyls were found in quantifying quantities in all the samplers, with formaldehyde having the highest concentrations.

After comparing the concentrations of the targeted pollutants in indoor and outdoor air, and calculating the Indoor/Outdoor Ratio, it was concluded that there are indoor sources for the compounds of interest in all the offices.

A correlation between concentration and indoor temperature and humidity couldn't be established due to a lack of variations in offices indoor air of the two parameters.

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