

INDOOR AIR EXPOSURE TO ALDEHYDES AND KETONES IN ROOMS WITH NEW AND OLD FURNITURE OF A NEW OFFICE BUILDING

R. DIODIU^{a,b*}, E. BUCUR^{a,c}, T. GALAON^a, L. F. PASCU^a

^a*National Research and Development Institute for Industrial Ecology – INCD ECOIND, 71–73 Drumul Podu Dambovitei Street, 060 652 Bucharest, Romania
E-mail: poluare.aer@incdecoind.ro; raluca_dio@yahoo.com*

^b*Faculty of Environmental Science and Engineering, Babes-Bolyai University, 30 Fantanele Street, 400 294 Cluj Napoca, Romania*

^c*Department of Analytical Chemistry, University of Bucharest, 90–92 Panduri Street, 050 657 Bucharest, Romania*

Abstract. The aim of this article was to evaluate and compare the levels of aldehydes and ketones in indoor air of a new office building in rooms with new and old furniture. The sampling method involved both passive cartridges and silica gel DNPH-coated tubes. Aldehydes and ketones levels were quantified using a DNPH-derivatisation method followed by liquid chromatography coupled to UV detection for 14 aldehydes and ketones. The results obtained showed that both active and passive sampling methods can be used for indoor air aldehydes and ketones assessment depending on what you intend to achieve: long-term average or short-term monitoring. Results revealed that higher concentrations of aldehydes and ketones were found in rooms with new furniture compared to rooms with relative old furniture, making new furniture a possible source of aldehydes and ketones.

Keywords: indoor air, DNPH-derivatisation, aldehydes, ketones, HPLC.

AIMS AND BACKGROUND

Today, more than ever, we are confronting with an increase in health problems due to indoor air quality as a consequence to the huge time spent indoor. The average time spent at work by people working in an office building revolves around eight and a half hours to nine hours and even more in a five-day working week. To this time spent indoor at work is added the time spent at home for rest, household chores and recreation.

Main effects on human health of carbonyls described in literature are like primary irritation of the mucous membranes of the eyes, the upper respiratory tract, and the skin.

Indoor air sources of carbonyls in offices buildings include building materials, plywood, adhesives, laminate floorings, paints and solvents. In addition, it

* For correspondence.

was proved that new materials and new buildings tend to emit more pollutants in air than old ones¹. Carbonyl compounds can occur in the indoor environment as secondary emissions, therefore as products of the reaction of a primarily emitted pollutant with ozone².

Numerous studies on the targeted carbonyl compounds on indoor air were conducted since '90s until present times. Indoor carbonyl concentrations have been measured in many countries, in Europe and around the world such as offices³⁻⁵, residences⁶⁻⁸, schools and kindergartens⁹⁻¹¹. Also, studies realised on outdoor air quality in important cities and overall emissions from Romania showed the possibility presence of carbonyls as VOC and NMVOC in outdoor air^{12,13}.

The most efficient methods for indoor air measurements of carbonyls involve active or passive sampling methods for air and retaining carbonyl compounds by adsorption on solid adsorbents impregnated with DNPH, extraction of the derivatised product in acetonitrile and chromatographic analysis by HPLC coupled to UV detection. The scheme of the derivatisation process is shown in Fig. 1. It is recommended that an ozone scrubber to be installed prior to the DNPH cartridge since ozone interferes with the carbonyl-DNPH (Ref. 14).

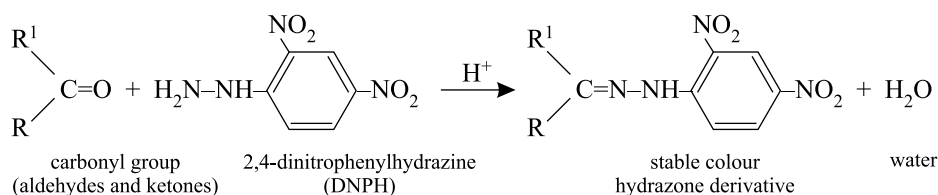


Fig. 1. Chemical reaction for derivatising of carbonyls from air samples¹⁴

The aim of this study was to evaluate the indoor air quality regarding aldehydes and ketones from a new office building located on the outskirts of Bucharest. In order to do that, indoor air from selected rooms was collected on passive and active cartridges for carbonyl derivatisation. Our purpose was to see if there are any differences regarding the concentration of the interested carbonyls in the rooms that have relative old furniture, a couple of years old, and rooms that have new furniture brought just 2 months ago. We also wanted to see how the outdoor (ambient air) levels for the targeted carbonyls were, and to compare them with the indoor results. Doing so, we could establish if there are some major indoor sources of carbonyls from indoor air or the outdoor air is a main source of these pollutants indoor.

EXPERIMENTAL

Sampling was conducted in a new office building located on the outskirts of Bucharest (capital of Romania). The building has six floors above ground and one

floor underground. Construction of the building was completed in autumn 2011. Furniture for the offices was bought in 2009 and moved in the new building; also new furniture was bought in the beginning of 2015 for a few offices. Sampling was done in rooms with old and rooms with new furniture (Table 1).

Table 1. Constructive and functionality properties of the rooms tested

Office (sample name)	Activities/equipments/furniture	Floor	V (m ³)	Number of persons	Occupancy rate (m ³ /habitant)
A1	office activities/6 computers, copy machines/old furniture	3	91.50	6	15.25
A3	office activities/10 computers, copy machines/new furniture	1	211.52	10	21.15
A4	office activities/1 computers, copy machines/new furniture	1	66.88	1	66.88
A5	office activities/2 computers, copy machines/old furniture	5	57.60	2	28.80

Sampling campaign was done from 2nd to 11th of March 2015. In order not to disturb the working personal and also according with the best time to sampler for indoor carbonyls in literature, all the active samplings were done at night time, starting at the end of the work program until 8 AM next morning.

Carbonyls were analysed and determined according to US-EPA methods TO-11A and IP-6 and sampled according to US EPA 0100 (Refs 14–16). The compounds were collected by passive and active sampling, and included sampling devices in which the derivatisation process also took place with DNPH. For passive sampling were purchased LpDNPH cartridges design for sampling carbonyls in indoor from Sigma-Aldrich. Active sampling for indoor and ambient air was done on ORBO™-555 6 mm O.D. × 110 mm length dual-layer DNPH glass sampling tubes. In order to eliminate ozone interference a potassium iodide (KI) ozone scrubber was connected upstream the cartridge. Sampling flow was set at 1.0 l min⁻¹. Passive and active cartridges were extracted in 5 ml volumetric flask with acetonitrile.

All the samplers were analysed within ten days from their sampling. Both active and passive DNPH cartridges were measured by the same analysis method, despite the concentrations were calculated, respectively. As a calibration standard TO11/IP-6A Aldehyde/Ketone-DNPH Mix certified reference material with 15 µg/ml concentration of each carbonyl in acetonitrile was used. The calibration standards contained hydrazones of the following 15 carbonyl compounds: acetaldehyde, acetone, acrolein, benzaldehyde, butyraldehyde, crotonaldehyde, 2,5-dimethylbenzaldehyde, formaldehyde, hexaldehyde, isovaleraldehyde, propionaldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, valeraldehyde.

The determinations of interested carbonyls compounds was done by a high performance liquid chromatograph model Agilent 1200, coupled with a UV detector, at 365 nm wave length. The analytical conditions were: two Zorbax Eclipse C18 reversed-phase columns (250 mm, 4.6 mm, 5 μ m); isocratic mobile phase: acetonitrile/water (acetonitrile: HPLC grade; water: HPLC grade); flow rate 2 ml min^{-1} ; sample injection volume 25 μ l; column temperature 25°C.

The elution gradient was as follows: upon sample injection, linear gradient from 60 to 75% acetonitrile/40 to 25% water in 30 min, linear gradient from 75 to 100% acetonitrile/25 to 0% water in 20 min, hold at 100% acetonitrile for 5 min, reverse gradient to 60% acetonitrile/40% water in 1 min, and maintain isocratic at 60% acetonitrile/40% water for 15 min (Ref. 15).

The carbonyl concentrations were quantified by external standard calibration. The calibration curves covered the range of interest and showed good linearity, with $R^2 > 0.999$ for all the carbonyls except 2,5-dimethylbenzaldehyde ($R^2 > 0.996$).

As also found by Jiang et al.¹, the traditional DNPH method is unsuitable for separating and determining acrolein from acetone. The mentioned aldehydes can be determined and separated by other analytical method specialised for each pollutant in air matrix, like the methods from the National Institute for Occupational Safety and Health (NIOSH): NIOSH Acrolein 2501 Method for the determination of acrolein¹⁷ and NIOSH Ketones 1 1300 Method for the determination of acetone¹⁸. Concentrations of the mentioned carbonyls will be referred as acrolein + acetone in this study.

RESULTS AND DISCUSSION

The results obtained for passive and active sampling in all the offices are shown in Table 2, far an easy comparison, the results for the outdoor concentrations are also shown in the same table.

According to the results, the highest concentration of carbonyls was found in office A3. This is an office with new furniture and 10 people working, similar with an open space working area. In office A3, the carbonyls concentrations were much higher than all the other studied sampling sites. Not all the offices presented the same pattern, the other office with new furniture had similar concentrations with the ones with old furniture.

Comparing the total amount of carbonyls, the room with the lower concentrations was A4. This office has the largest space based on occupancy rate for the people working there. Even if A1 had lower concentrations of formaldehyde than A4, the cleanest air, based on our results is found in office A4.

Indoor/outdoor ratio (I/O) was mainly above 1, suggesting indoor sources of carbonyls for the concentration found in indoor air or, at least, that indoor sources are higher in terms of pollutants emissions than the ones from outdoor air. This was observed in all the carbonyls except acrolein and acetone.

Table 2. Concentrations of carbonyl compounds in selected offices in 2015

Carbonyl compounds	A1		A3		A4		A5		Outdoor			
	active µg/m ³	I/O	active µg/m ³	passive µg/m ³	active µg/m ³	passive µg/m ³	active µg/m ³	passive µg/m ³	active µg/m ³	passive µg/m ³		
Formaldehyde	0.40	≈1	26.00	>1	1.89	>1	1.23	>1	21.49	>1	18.25	0.34
Acetaldehyde	1.07	>1	14.65	<1	1.20	>1	0.35	≈1	10.25	>1	8.35	0.29
Acrolein + acetone	21.43	≈1	13.41	≈1	2.15	<1	12.54	<1	22.63	≈1	10.78	21.21
Propionaldehyde	0.87	>1	2.28	>1	0.33	>1	1.02	>1	1.16	>1	1.25	0.03
Crotonaldehyde	0.09	>1	0.17	>1	0.02	≈1	—	—	0.15	>1	—	0.02
Butyraldehyde	2.30	>1	1.34	>1	0.11	>1	—	—	0.92	>1	—	0.02
Benzaldehyde	0.52	>1	0.96	>1	0.06	≈1	—	—	0.79	>1	—	0.02
Isovaleraldehyde	0.05	≈1	0.79	>1	0.05	≈1	—	—	0.46	>1	—	0.03
Valeraldehyde	1.97	>1	2.10	>1	0.24	>1	—	—	1.01	>1	1.58	0.01
<i>o</i> -Tolualdehyde	1.80	>1	0.36	>1	0.01	<1	—	—	0.15	>1	0.89	0.07
<i>m</i> -Tolualdehyde	3.04	>1	0.06	≈1	0.04	≈1	—	—	0.04	≈1	—	0.04
<i>p</i> -Tolualdehyde	1.37	>1	0.43	>1	0.02	≈1	—	—	0.16	>1	—	0.05
Hexaldehyde	0.22	>1	8.59	>1	0.93	>1	—	—	3.42	>1	2.13	0.02
2,5-Dimethylbenzaldehyde	0.40	>1	0.42	>1	0.41	>1	—	—	0.43	>1	—	0.13
∑ carbonyls	35.64	>1	71.80	>1	7.52	<1	—	—	63.30	>1	—	22.31

I/O – indoor/outdoor.

The concentrations found for acrolein and acetone were higher than other carbonyls concentrations in every sample analysed. Also, I/O ratio for acrolein and acetone was close to 1 or smaller than 1. Based on the high concentration found and the I/O ratio, in the case of acrolein and acetone, we suggest that the main source of these carbonyls could be found in outdoor air.

Sampling cartridges both passive and active were dedicated for carbonyls sampling and derivatisation, being successfully used in determining indoor carbonyls levels in selected offices. Results from passive cartridges followed the same pattern as the concentrations determined in the active cartridges for all the sampling points.

CONCLUSIONS

From all the sampling rooms with old and new furniture that were analysed, the highest concentration of carbonyls was found in an office with new furniture; the other offices tended to have similar and smaller concentrations of carbonyls. Acrolein and acetone had the higher concentrations found and their concentration in the outdoor air suggested an outside the building potential source of this carbonyl. Concentration found in passive samplings were relatively similar with ones determined with active sampling, but further research in this matter will need to be carried in the future.

Acknowledgements. The tests have been done inside the Program Nucleu financed by the Ministry of Education and Research of Romania whom we thank with this opportunity for all the support.

REFERENCES

1. C. JIANG, P. ZHANG: Indoor Carbonyl Compounds in an Academic Building in Beijing, China: Concentrations and Influencing Factors. *Front Environ Sci Eng*, **6** (2), 184 (2012).
2. D. A. SARIGIANNIS, S. P. KARAKITSIOS, A. GOTTI, I. L. LIAKOS, A. KATSOYIANNIS: Exposure to Major Volatile Organic Compounds and Carbonyls in European Indoor Environments and Associated Health Risk. *Environ Int*, **37**, 743 (2011).
3. A. BÁEZ, H. PADILLA, R. GARCÍA, M. C. TORRES, I. ROSAS, R. BELMONT: Carbonyl Levels in Indoor and Outdoor Air in Mexico City and Xalapa, Mexico. *Sci Total Environ*, **302** (1–3), 211 (2003).
4. W. LIU, J. ZHANG, L. ZHANG, B. J. TURPIN, C. P. WELSEL, M. T. MORANDI, T. H. STOCK, S. COLOME, L. R. KORN: Estimating Contributions of Indoor and Outdoor Sources to Indoor Carbonyl Concentrations in Three Urban Areas of the United States. *Atm Environ*, **40** (12), 2202 (2006).
5. M. ONGWANDEE, R. MOONRINTA, S. PANYAMETHEEKUL, C. TANGBANLUEKAL, G. MORRISON: Concentrations and Strengths of Formaldehyde and Acetaldehyde in Office Buildings in Bangkok, Thailand. *Indoor Built Environ*, **18** (6), 569 (2009).
6. B. CLARISSE, A. M. LAURENT, N. SETA, Y. Le MOULLEC, A. El HASNAOUI, I. MOMAS: Indoor Aldehydes: Measurement of Contamination Levels and Identification of Their Determinants in Paris Dwellings. *Environ Res*, **92** (3), 245 (2003).

7. C. MARCHAND, B. BUILLOT, S. Le CALVE, P. MIRABEL: Aldehyde Measurements in Indoor Environments in Strasbourg (France). *Atm Environ*, **40** (7), 1336 (2006).
8. C. MARCHAND, S. Le CALVE, P. MIRABEL, N. GLASSER, A. CASSET, N. SCHNEIDER, F. De BLAY: Concentrations and Determinants of Gaseous Aldehydes in 162 Homes in Strasbourg (France). *Atm Environ*, **42** (3), 505 (2008).
9. H. FROMME, D. HEITMANN, S. DIETRICH, R. SCHIERL, W. KORNER, M. KIRANOGLU, A. ZAPF, D. TWARDELLA: Air Quality in Schools – Classroom Levels of Carbon Dioxide (CO₂), Volatile Organic Compounds (VOC), Aldehydes, Endotoxins and Cat Allergen. *Gesundheitswesen*, **70**, 88 (2008).
10. O. GEISS, G. GIANNOPOULOS, S. TIRENDI, J. BARRERO-MORENO, Br. LARSEN, D. KOTZIAS: The AIRMEX Study – VOC Measurements in Public Buildings and Schools/Kindergartens in Eleven European Cities: Statistical Analysis of the Data. *Atm Environ*, **45**, 3676 (2011).
11. N. KALINIC, K. SEGA: Relationship between Summer and Winter Formaldehyde Levels in Kindergartens and Primary Schools. *Environ Manage Health*, **7**, 21 (1996).
12. C. CERCELARU, I. IONEL, I. VETRES: Air Pollution Analysis Established by a DOAS System. *J Environ Prot Ecol*, **15** (2), 395(2014).
13. O. FALUP, I. MIRCEA, R. IVAN, I. IONEL: Novel Approach for the Current State of Greenhouse Gases Emissions. Romanian Case Study. *J Environ Prot Ecol*, **15** (3), 807 (2014).
14. United States Environmental Protection Agency (US EPA): Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) (EPA-625/R-96/010b), Compendium Method TO-11A; Centre for Environmental Research Information, Cincinnati, OH, USA, 1997.
15. SKC EPA IP-6 Method Update: Determination of Formaldehyde and Other Aldehydes in Indoor Air. 2004.
16. United States Environmental Protection Agency (US EPA): Method 0100, Sampling for Formaldehyde and Other Carbonyl Compounds in Indoor Air. 1996.
17. National Institute for Occupational Safety and Health (NIOSH): Acrolein Method 2501, NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 1994.
18. National Institute for Occupational Safety and Health (NIOSH): Ketones 1 Method 1300, NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 1994.

Received 9 June 2015

Revised 23 June 2015