

Alternative method for the measurement of formaldehyde and carbonyl compounds in indoor environments

Delphine BOURDIN^{1,2}, R&D Engineer/PhD Student and Valérie DESAUZIERS¹, Assistant-Professor

¹ *Laboratoire Génie de l'Environnement Industriel – Ecole des Mines d'Alès (site de Pau) – Hélioparc, 2 avenue Pierre Angot – 64000 Pau, France*

² *Nobatek – 67 rue de Mirambeau – 64600 Anglet – France*

Formaldehyde is a pollutant frequently found in the indoor environments because of its numerous sources including building materials¹. Since 2004, it has been classified as “Carcinogenic to humans” by the International Agency for Research on Cancer (IARC) and the French Agency for Food, Environmental and Occupational Health and Safety (ANSES) recommends a guide value for indoor air in case of long term exposures of 10 $\mu\text{g}\cdot\text{m}^{-3}$. Thus, it is important to have sensitive analytical methods allowing to detect and to quantify formaldehyde in indoor environments. The standardized method widely used consists in sampling formaldehyde on adsorbent tubes impregnated with 2,4-dinitrophenylhydrazine (2,4-DNPH). The resulting carbonyl derivatives are then desorbed with acetonitrile and analyzed with HPLC/UV. Capillary GC presents a better resolution than HPLC and, coupled with mass spectrometry, allows the characterization of all the compounds in a sample. In addition, solid phase microextraction (SPME) is a sensitive and easy-to-use sampling method which can be easily applied to on-site applications^{2,3}. Consequently, in order to have a simpler sampling and analysis tool allowing a full screening of aldehydes in the air, we developed an analytical method involving on-fiber derivatization followed by GC/MS analysis after direct thermal desorption in a classic injection port. The first step of this development consisted in loading the fiber with a derivatization reagent. In this aim two reagents were selected: pentafluorophenylhydrazine⁴ (PFPH) and o-(2,3,4,5,6 pentafluorobenzyl) hydroxylamine⁵ (PFBHA), and three different fiber coatings were considered (PDMS/Carboxen, PDMS/DiVinylBenzene and PDMS/Carboxen/DiVinylBenzene). The fiber loading was carried out by simple exposure to the headspace of a sealed vial containing pure reagents or reagents in aqueous solutions. According to the volatility of the reactant, the vial can be previously heated in order to improve the impregnation yield. The loading time was optimized from the kinetics obtained for each fiber and each reagent.

Concerning PFPH, 30 minutes were necessary to reach the equilibrium state on a PDMS/Carboxen/DVB fiber and 20 minutes with a PDMS/DVB fiber. Finally, the PDMS/Carboxen fiber was not retained due to the on-fiber degradation of the reagents during the thermal desorption step. For PDMS/DVB fiber, the maximum amount of derivatization reagent loaded was 200 nmol, corresponding to a maximum quantity of 6 μg of formaldehyde. For the PDMS/DVB fibers, the repeatability of the loading on a same fiber was 4.4% (n=6) and the reproducibility from one fiber to another one was 7.8% (n=3).

Concerning PFBHA, the loading was made from an aqueous solution previously stirred. The same problem than with PFPH was observed with Carboxen coatings: the degradation of the reagents during the thermal desorption step. Thus, the PDMS/DVB fiber was chosen. The maximum amount of derivatization reagent loaded was 420 nmol, the repeatability of the loading on a same fiber was 7.9% (n=6) and the loading equilibrium was reached after 20 minutes. The conservation yield of the reactant loaded onto the fiber was greater than 75% after three days at room temperature.

Standard atmospheres of formaldehyde were then generated using a permeation device in order to determine the performance of the method in terms of limit of detection, linearity, repeatability and reproducibility. Thus, with a 20 minute sampling time, the limit of detection in GC/FID reaches 0.9 $\mu\text{g}\cdot\text{m}^{-3}$. Besides, the conservation of the sample once the formaldehyde was derivatized onto the fiber is possible during 3 days at room temperature. Moreover, this method can be applied to other carbonyl compounds potentially present in indoor air. This analytical method, in combination with the analysis of VOCs previously developed in our laboratory, will be further extended to the characterization of building material emissions and to the evaluation of indoor air quality.

¹ A.T. Hodgson, D. Beal, J.E.R. McIlvaine, *Indoor Air*, 12, 235 (2002)

² V. Larroque, V. Desauziers and P. Mocho, *J. Environ. Monit.*, 8, 106 (2006)

³ V. Larroque, V. Desauziers and P. Mocho, *Anal Bioanal Chem*, 386, 1457 (2006)

⁴ Y.-C. Chien and K.-G. Yin, *J. Environ. Monit.*, 11, 1013 (2009)

⁵ P.A. Martos and J. Pawliszyn, *Anal. Chem.*, 70, 2311 (1998)