

Assessment of the exposure to formaldehyde while driving: a feasibility study

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Abstract

In this paper we demonstrate the feasibility of formaldehyde quantification inside a moving vehicle. This allows assessing the exposure of driver and passengers to this allergenic and carcinogenic pollutant in real driving conditions, and exploring the origin of the formaldehyde measured inside the vehicle. Part of the formaldehyde may be intrinsically emitted by the materials inside the car, such as plastics or fabric, therefore strongly depending on the temperature and humidity conditions, but we have to consider formaldehyde coming from outside air entering the vehicle, which is dominated by the emissions in the exhaust gases of surrounding vehicles.

Keys-words: *air pollution, in-vehicle air, people exposure, formaldehyde, on-road analysis.*

Résumé

Dans ce travail nous démontrons la possibilité de quantifier le formaldéhyde dans un véhicule pendant son utilisation. Ceci permet d'évaluer l'exposition du conducteur et des passagers à ce polluant allergénique et cancérigène dans des conditions réelles, et d'explorer l'origine du formaldéhyde dans l'habitacle. Une partie du formaldéhyde peut être émis par les matériaux du véhicule, comme les plastiques ou les tissus, et donc serait très dépendant des conditions de température et d'humidité. Cependant, le formaldéhyde peut également provenir de l'air extérieur entrant dans le véhicule, qui est dominé par les émissions dans les gaz d'échappement des véhicules alentour.

Mots-clefs: *pollution de l'air, air de l'habitacle, exposition des personnes, formaldéhyde, analyse en conditions réelles.*

1. Introduction

In spite of the relatively small concentration of formaldehyde measured in the air, typically 1 to 10 ppbv in urban environment, and less than 1 ppbv in rural air, formaldehyde is nowadays a target component of air pollution studies, because its adverse sanitary effects have been recognized, because it is a key species in the atmospheric chemical system, and because it is an ubiquitous pollutant, in particular in confined environments, where concentrations above 100 ppbv are not unusual. Formaldehyde is indeed widely used for industrial applications and is emitted by many materials such as plastics, fabric, solvents..., though the emissivity of these materials is not yet fully determined. Another major source of formaldehyde is combustion, and specifically the emissions of formaldehyde by vehicles have been also widely studied, in relation to the general outdoor air quality.

Vehicles constitute a small volume micro-environment where pollutants, and in particular aldehydes, can have many sources: indoor material emissions, gasoline loss and exhaust leakage (self-pollution), and infiltration of outdoor air. Additional sources of pollutants are related to potential photochemical formation inside the car, as well as the habits of the driver and passengers, namely smoking, the use of air fresheners (Lamorena & Lee (2008))... However, the assessment of air quality inside vehicles and the exposure of people in this environment is comparatively a recent field of research. The first studies investigated the levels of VOCs, CO, PM, ozone and NO₂ inside

vehicles (see for instance Chan et al. (1991)). A specific interest was developed for formaldehyde measurements inside cars by Jo & Lee (2002) after the initial work of Rodes & al. (1998), but still the number of studies where formaldehyde is quantified inside vehicles remains scarce. Lawryk et al. (1995) reported results during commutes on the New Jersey and New York City area, Rodes et al. (1998) and Sabin et al. (2005) studied the exposure of persons in California, and Jo & Lee (2002) in Taegu, Korea, Shiohara et al. (2005) in Mexico City, Pang & Mu (2007) and Zhang et al. (2008) in Beijing. These studies showed that the formaldehyde concentration inside the vehicle is much higher than the outdoor concentration, that intake from outside air through the hood, the windows or the vents is important, so that the formaldehyde concentration inside is strongly dependent upon the traffic conditions, and upon the vehicle that is followed. Another important factor seems to be the temperature inside the car and the temperature difference between indoor and outdoor air.

Considering the differences in the vehicles, in the gasoline composition, in the geographical and meteorological conditions, the results obtained in these studies cannot be extrapolated to other countries. We have tried to address this lack of data regarding the French car fleet, using the infrared tunable diode laser spectrometer, originally designed for the real-time quantification of formaldehyde at trace level in outdoor air. As the spectrometer cannot be installed into a vehicle, we have developed a specific sampling procedure, followed by analysis of the samples in the laboratory. Our method is an alternative to the standard aldehydes quantification by sampling on DNPH cartridges and subsequent analysis by UV-HPLC.

2. Analysis and sampling methodology

2.1. Formaldehyde quantification by infrared diode laser spectroscopy

The spectrometer used for the quantification of formaldehyde is fully detailed in Dusanter et al. (2002) and will only be briefly described here. It is represented on Figure 1. The infrared radiation emitted by a tunable liquid-nitrogen-cooled lead-salt laser is actively stabilized on a formaldehyde absorption line around 2829 cm^{-1} . The 30 meter absorption cell initially under vacuum is filled with the sample to analyse up to about 12 Torr. The absorption signal S is recorded during this step together with the pressure. The slope at origin of the resulting S vs. P curve is proportional to the molar fraction of formaldehyde inside the sample. Absolute calibration of the spectrometer response is provided by a permeation system delivering a known formaldehyde concentration. Uncertainty in the measured concentration is about 10%. Comparison of the performance of the spectrometer with the standard UV-HPLC analysis of samples collected on DNPH cartridges has been established in a former study on the quantification of formaldehyde in libraries (Hanoune et al. (2006)).

2.2. Sampling methodology

Air samples from inside the vehicle are collected into 10L Tedlar bags using PTFE tubing and a KNF™ sampling pump when working on vehicles at rest. For on-road experiments, a Rakoon™ air inflator powered by the car 12V electrical system was used (Figure 2). Sample collection takes about two minutes. Air was sampled in the front passenger breathing zone, but it is assumed that the concentration is homogeneous inside the entire passenger compartment, as discussed by Lawryk et al. (1995).

The volume collected in the Tedlar bags is amply sufficient for a repeated analysis of the sample, as only 0.2L of sample material at atmospheric pressure is needed for the formaldehyde quantification. This allows to repeat the analysis several times, and to check the stability over time of the sample inside the Tedlar bag, as had been done in our previous work (Hanoune et al. (2006)). The formaldehyde concentration in the sample bag does slowly evolve over several days and tends to equilibrate with the formaldehyde concentration in the room where the bag is stored. The initial formaldehyde concentration can be determined directly if the analysis is performed less than an hour after the collection of the sample. Alternatively, the initial concentration can also be extrapolated from the time series of the concentration measurement for one bag.

In the present study, the analysis of the samples were made within an hour after sampling, so as to eliminate the risk of sample evolution, because the concentrations of formaldehyde are quite low, even lower than the laboratory concentration of 6 to 8 ppbv.

2.3. Car fleet

The vehicles under study here are not representative of the French fleet, but were chosen for their availability. Both Diesel and gasoline powered cars were tested, as well as new and old cars, compact and mid-sized cars. No specific attention was taken to the general state or cleanliness of the cars.

3. Validation in simulated and real traffic conditions

3.1. Formaldehyde background concentration in vehicles at rest

A first set of experiments was performed in winter (external temperature around 0 °C) on vehicles at rest on a parking lot close to the laboratory. Air samples were collected using the KNF pump placed inside the car, with the air inlet in the breathing zone of the front passenger. To reproduce the normal air-tightness of the car, the electrical power cord was pinched in the door of the car. Alternate measurements were perfumed with the sampling Teflon tubing entering the car through the window. No significant differences were noted in the analysis of the samples using the two methods, as expected when we consider the short time needed for the sample collection.

The results are displayed in Figure 3. There is, as expected, a low background concentration of formaldehyde inside the cars, with individual variations in the range 0.6 to 6.9 ppbv. This concentration range is similar but exceeds the concentration of formaldehyde in the outside air, which was measured simultaneously and ranges from 1 to 3 ppbv. The lowest concentrations of formaldehyde inside the cars were found for vehicles that had been at rest on the parking lot for a longer time. One measurement gave a value of 15.5 ppbv, even though the vehicle had been at rest for a few hours. This was attributed to the nearby presence of an air conditioning exhaust, and the experiment, performed anew one hour later on another parking spot, led to a concentration of 2 ppbv, within the range of the other data.

3.2. Simulated traffic conditions

Traffic conditions were crudely simulated using two vehicles. The first one acted as the pollution source, and was placed about two meters in front of the vehicle under investigation. The polluting vehicle underwent irregular accelerations to 2000-3000 rpm, so as to approach the conditions of urban dense traffic. The second vehicle was at rest. The wind speed was not measured, but the direction of the wind was not in the axis of the cars, leading to only a fraction of the exhaust gas going in the direction of the second car.

When the leading vehicle was Diesel fuelled, two sets of experiments were performed, to test for the venting and heating conditions. With the vents closed and no heating in the vehicle under test, though unrealistic conditions in winter, formaldehyde concentrations measured inside the car climbed from 2.8 ppb before the experiment, which corresponds to the outdoor formaldehyde concentration, to 10 ppbv after 10 minutes. Formaldehyde was also measured on the hood of the test car, to evaluate the exhaust emissions of the polluting car, with a value of about 25 ppbv. With the heating system on, the indoor concentration measured climbed from 2 ppbv to 33 ppbv, independently on the state of the venting system, and formaldehyde concentration above the hood was 13.4 ppbv. These is however no way of determining so far whether the concentration levels measured on the hood come solely from the exhaust of the front vehicle, or also from formaldehyde possibly emitted by the engine.

When the polluting vehicle was gasoline fuelled, the concentration climbed from 0 to 7 ppbv only.

These preliminary experiments show that the formaldehyde coming from outside is a major source of pollution inside the car, as was already found in previous studies, and that the heating system also generates or propagates formaldehyde inside the car.

3.3. On-road measurements

A last set of experiment was performed in one vehicle moving in the Lille area, and sampling was done with the Rakoon™ pump in three completely different situations. Formaldehyde concentrations measured in this configuration range from 4.7 ppbv on the covered parking lot of a mall, to 16.6 ppbv during a stalled traffic situation at a highway interchange, with intermediate concentration of 11.1 ppbv when stopping at a traffic light, close to a visibly polluting Diesel truck. This set of experiments illustrates the quick variability of the formaldehyde concentration, as the total time for the 3 measurements was only 18 minutes, and the possibilities of our sampling and analysis system to monitor these short term variations.

4. Discussion

The aim of the present study was only to validate the methodology to quantify formaldehyde in real traffic conditions. Significant data could only be obtained on a much more consequent number of vehicles, which would ideally be representative of the French fleet. A thorough study would also require the systematic analysis of the formaldehyde concentration by the side of the road, as was done in other studies (for instance Pang & Mu 2007). However, a few remarks can be made concerning the observed levels of formaldehyde inside the vehicles, and its origin.

The background formaldehyde concentration inside the vehicles measured in winter is low and comparable to the outdoor concentration, and seem to decrease with the length of time the car has been at rest. A couple of measurements after a short drive led to concentrations in the cars of about 20 ppb. This would indicate that all sources of formaldehyde are temperature dependent, and that air exchange between indoor and outdoor is a major factor. This effect is further demonstrated by the one experimental result that we rejected on cars at rest, where the concentration of formaldehyde inside the car was measured to be 15.5 ppbv, even though the vehicle had been at rest for a few hours, which was attributed to a nearby air conditioning exhaust pipe. The influence of air exchange between the interior of the car and the surrounding air is further demonstrated in the on-road experiments, where the rapid variations of formaldehyde concentration inside the car can be solely attributed to the exterior factors, i.e. the local air pollution and therefore the traffic conditions.

The effect of outside temperature on the pollution levels inside cars has been the object of debate. Results from Jo & Lee (2002) do not agree with our observations, though other studies do, such as the work of Weisel et al. (1992). Jo & Lee (2002) only discuss the external formaldehyde contribution of the self-pollution by the emission of the car, but the discrepancies could also be attributed to internal factors related to the materials of the car, or to the heating of the car, which is also supported by our results. The emission of formaldehyde by the articles inside the cars is discussed more in detail by Schupp et al. (2005), who extrapolated for instance concentrations of formaldehyde at 65°C (corresponding to a car parked in the sun) above 1000 ppbv. The seasonal effect is also described by Yoshida & Matsunaga (2006), who demonstrated at the same time the intrinsic emission of formaldehyde by new cars.

As to the main source of formaldehyde in the outdoor air, it is without any doubt linked to the emissions by the vehicles in the traffic. Our results indicate that Diesel cars produce more formaldehyde than gasoline cars. This is supported by other studies where a comparison of unregulated pollutants was made, such as the work of Caplain et al. (2006). Alternative fuels such as biodiesel blends would seem to reduce the emissions of formaldehyde, as presented by Peng et al. (2008), but not ethanol-blended fuel, as demonstrated by Pang et al. (2008)

5. Conclusion

This study demonstrates the feasibility of on-road formaldehyde quantification. This technique will possibly allow investigating the main parameters upon which depends the formaldehyde concentration inside a vehicle: outdoor air, self-emission, materials emissivity, heating, venting, fuel composition, vehicle eventual malfunction... This technique provides near-time resolved results, as it only necessitates small sampling time and small volume samples, which is not the case with conventional sampling on DNPH-impregnated cartridges and HPLC analysis. With the rapid

response of the technique, it will be easier to determine the contribution of each of the sources of formaldehyde, in controlled conditions, as well as during road experiments.

These first experimental results on the formaldehyde concentrations inside vehicles in France agrees in general with the data collected in other countries.

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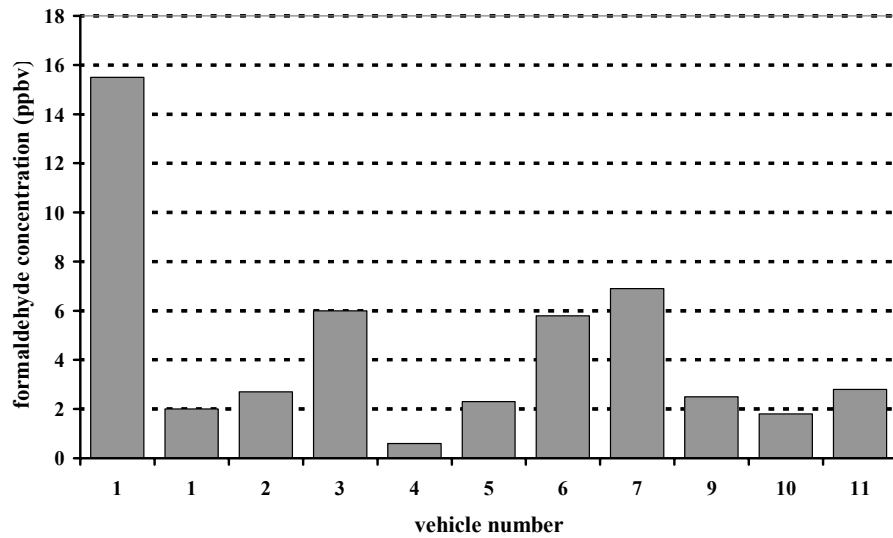


Figure 3: Formaldehyde concentration in cars at rest. For vehicle #1, the first value corresponds to the measurement performed when the car was under the influence of an air conditioning outlet, the second value when it was away from the outlet.



Figure 1: View of the infrared tunable diode laser spectrometer used for the quantification of formaldehyde.



Figure 2: View of the in-car sampling system.