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## ***Interactive comment on “Analysis of non-regulated vehicular emissions by extractive FTIR spectrometry: tests on a hybrid car in Mexico City” by F. Reyes et al.***

**F. Reyes et al.**

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1) With respect to the reviewer’s comment on the lack of novelty in this contribution, in the literature there has been very few peer-reviewed articles published in which FTIR spectrometry is used to characterize car emissions. The current experimental set-up is being applied to measure the exhaust of a hybrid car for the first time and offers relevant discussions in the process of choosing the correct parameters for good speciation capability with respect to fast response times. The capability of performing quality tests of vehicular emissions by this laboratory is reflected in this first article which attempts to be precise in the description of the methodology. Forthcoming contributions of this working group will report results of car fleets, or the effects of specific emission control systems and fuels, and will be able to cite this paper as a reference for the experimen-

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tal details. Also, in this publication driving cycles specifically designed for Mexico City are used for the first time and the results are compared to those from the more commonly used sequences. The results presented in this article show how locally defined conditions (i.e. driving cycles, gasoline types and atmospheric parameters) are crucial when deriving emission factors. Significant differences when comparing the emission results when different driving cycles are run suggest that great caution needs to be taken before adopting the values from studies carried out in other countries. Therefore, the authors believe that the material in this publication is relevant and important, especially when Mexico City has been chosen for international air quality studies such as MILAGRO.

2) The reviewer questions the insufficient justification for the use of FTIR spectrometry for vehicular exhaust monitoring and correctly points out that the system described here cannot be considered as inexpensive when compared to other techniques. The authors accept this comment and the text will be changed as to more accurately define the advantages both of this methodology and of the more commonly available methods. The costs of performing FTIR analysis of exhaust gases is not low, but comparable or lower to those when individual instruments needed to analyze all these gases are considered. For some of these gases, the quantitative analysis would involve sample-taking and subsequent analysis in the lab. An important advantage is the calibration, which is inherent in the spectroscopic measurement and thus involves more infrastructure, work and attention when using other techniques. Another important contribution which reduces costs considerably without compromising accuracy is the Pitot-based flow measuring system proposed here. It consists of a low-cost differential pressure sensor, a Pitot tube, a thermocouple and an easy-to-use signal acquisition device and software built for this specific application. A commercial system for registering flow rates at the exhaust, usually based on the ventury principle, typically runs around \$15K USD. The manuscript will be modified accordingly as to clarify these points.

3) Losses are minimal considering the small amount of water condensed in the trap

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when compared to that passing across the cell. The trap's function is primarily to control and stabilize the pressure within the cell. If we consider one set of experiments in which tests were run for 81 min (1 MCMA sequence and 2 FTPs), the water collected in the trap was 12 ml. The water quantified in the cell from its IR absorptions and integrated along the 81 min was approx 145 grams. The condensed volume represents 7.7% of the total. The temperature, as result of an adiabatic expansion at the position of the valve, does not drop below 60°C. We do think that there is condensation at the position of the valve but the higher temperatures of the stainless-steel line (15 cm long) connecting the valve with the cell (180°C) will re-evaporate the drops along the way liberating NH<sub>3</sub> and CH<sub>3</sub>OH for detection. In order to be sure, we have calculated the amount of ammonia trapped in the 12 mL of condensed water. If the system was in equilibrium, the total amount of moles passing through the trap given P, V, R and T is  $n=0.3784$  mol. From that and the amount of ammonia present we could estimate its partial pressure  $P(\text{NH}_3)=1.368\text{E-}4$  atm. Based on the equation for deriving Henry's Law constant of NH<sub>3</sub> (Shi et al. 1999) at 62 °C we have  $H(\text{NH}_3)=8.82$  M atm<sup>-1</sup> and the amount held within the 12 mL of water collected would only be 3.16E-6 g. This amount is insignificant compared to the integrated 0.18 g of ammonia detected in the cell along the 81 min of tests. A comment will be added to the text with respect to the losses and the complete calculation could be included as supplemental information.

4) The response time under the given conditions is 20 s, as correctly commented by the reviewer. This corresponds to the system's response time rather than the spectrometer's response time since the flow-rate and the cell volume are the determining parameters. This clarification will be included in the manuscript. The system's response time of 5 s mentioned in the text, however, refers to an experiment in which the "White" cell was exchanged with one with smaller volume (0.75 L). This gas cell can be alternatively used when faster response times are needed.

5) The discussion of the data on Table 3 will be shortened. Only the significant findings will be included as suggested by the reviewer.

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6) At this point, it will be very difficult to do a fleet study of hybrid cars anywhere in the world. The hybrid technology just came available commercially in Mexico and at the time of the experiment there were 10 hybrids in Mexico. Only 9'500 hybrid vehicles were sold in the United States in the year 2000 and in 2005, the number (187'439) accounted to only 1.5% of the total of vehicles sold\*. Only about half a million are thought to be currently available in the whole world. Nevertheless, it is of great interest to the public and policy makers to have studies which evaluate the possible environmental benefits when adopting new technologies. It will be put clear in the manuscript that this contribution does not intend to have a representative fleet study but rather, focuses on the use of FTIR spectrometry for the analysis of various emission gases (many of which are non-regulated) not only for low emission vehicles tested on a the dynamometer, but also on-road and in larger sample sets, like it has recently been done in our lab.

7) As suggested by the reviewer, Fig. 2 will be moved to supporting information and the effect of spectral resolution and acquisition times will be briefly discussed in the text.

\* Business Week "News and Features", Dec. 18, 2005.

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5773, 2006.

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