

Nitrogen containing exhaust emissions for consideration in the aerosol research

P. Aakko-Saksa¹, T. Murtonen¹, P. Koponen¹, K. Lehtoranta¹, P. Roslund¹, P. Karjalainen², T. Rönkkö², H. Timonen³, S. Saarikoski³, R. Hillamo³.

¹VTT Technical Research Centre of Finland Ltd., P.O. Box 1000, FI-02044 VTT, Finland

²Tampere University of Technology, Department of Physics, FI-33720, Tampere, Finland

³Atmospheric Composition Research, Finnish Meteorological Institute, FI-00560, Helsinki, Finland

Keywords: ammonia, nitrogen oxides, secondary aerosol, traffic emissions.

Transformation of primary exhaust emissions into secondary products is an important aspect when traffic emissions are assessed. For example, about 30% of PM₁₀ measured is in the form of secondary inorganic sulphate and nitrate aerosols, which are formed from the transformation of gaseous SO₂, NO_x and NH₃ emitted from various sources. These aerosols are presumably even more important as regards PM_{2.5}. Secondary organic aerosols are formed from atmospheric oxidation and subsequent condensation of various VOCs (EEA 2012). Ammonia originates mainly from agricultural sources. However, concern of traffic sources in the production of ammonium aerosols increased as the use of urea-based SCR systems for NO_x control for diesel engines became common. Ammonia is also formed by the three-way catalysts of the spark-ignited gasoline cars. Nitrous oxide (N₂O), a strong greenhouse gas, is also induced by catalyst chemistry under lean conditions. (Meija-Centeno 2007, EEA 2012). In this study, an extensive set of emission constituents, including ammonia emissions, were measured from two flexible-fuel cars. These results are discussed in relation with nitrogen containing emissions from other types of internal combustion engines.

Emissions from two passenger cars (VW Passat MultiFuel, DISI engine, Ford Mondeo 2.0 FlexFuel, natural aspirated MPI engine) using fuels with different alcohol content (E10, E85, and E100) were measured on chassis dynamometer using the cold-start European exhaust emissions driving cycle (NEDC) and the hot-start FTP driving cycle. Several compounds were measured on-line using Fourier transformation infrared (FTIR) equipment (Gasmet Cr-2000) from the raw exhaust gas at two-second intervals. In-depth analyses of other emissions, also secondary organic aerosols were analysed in co-operation of three research organisations.

The NO_x emissions were low for the three-way catalyst (TWC) equipped spark-ignited cars in the NEDC tests. However, surprisingly high NO_x emissions were observed for the MPI car in the hot-start FTP test (up to 228 mg/km). The highest emissions are typically observed in the beginning of the cold-start test and during accelerations, whereas here the highest NO_x concentrations occurred in the hot-start FTP test after a 10 minutes pause. This

indicates engine adjustments optimised for low HC emissions leading to non-favourable conditions NO_x reduction (possibly lean air-to-fuel ratio). Nitrogen dioxide emissions were low (below 3 mg/km), as well as nitrous oxide emissions (below 5 mg/km). Both cars emitted quite similar emission levels of ammonia. The highest single emission result, close to 50 mg/km, was obtained for the the DISI car over the NEDC test cycle at -7 °C. High ammonia concentrations observed, typically over 10 ppm and substantial peaks up to 300-500 ppm. These ammonia concentrations are high when compared to limit value of 10 ppm for SCR equipped heavy-duty engines, for example. In theory, ammonia formation is enhanced in slightly rich air-to-fuel ratio at high temperatures (aggressive accelerations) when sufficiently HC and NO_x emissions are present (Li et al. 2010, Meija-Centeno 2007, Heeb et al. 2006). These results suggest that nitrogen containing emissions would deserve attention in the research of secondary aerosol formation for internal combustion engines.

This work was supported by Tekes within contribution in the IEA's Implementing Agreement on Advanced Motor Fuels (AMF) as Annex 44 (www.iea-amf.org/content/projects/annexes/44), and by the Academy of Finland (Grant No. 259016), Helsinki Energy, Ministry of Traffic and Communications, Tekes in the CLEEN/MMEA programme (WP4.5.2) and HERE and CENGE-projects (Tekes).

European Environment Agency. Air quality in Europe. EEA Report No 4/2012.

Heeb N.V., Saxer C.J. et al. Correlation of hydrogen, ammonia and nitrogen monoxide (nitric oxide) emissions of gasoline-fueled Euro-3 passenger cars at transient driving. Atmospheric Environment, Vol 40, 2006, pp. 3750-3763.

Li, W., Perry, K., Narayanaswamy, K., Kim, C. et al., Passive Ammonia SCR System for Lean-burn SIDI Engines, SAE Int. J. Fuels Lubr. 3(1):99-106, 2010, doi:10.4271/2010-01-0366.

Meija-Centeno, I., Martínez-Hernández, A. and Fuentes, G. Effect of low-sulfur fuels upon NH₃ and N₂O emission during operation of commercial three-way catalytic converters. Topics in Catalysis. Vols. 42-43, May 2007.