Gas phase sampling and determination of carbonyl compounds in ship diesel emissions: Differences between light fuel oil and heavy fuel oil operation

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Ship or marine transportation represents major conduit of international trade, and during the last decade the numbers of ships started to rise very quickly due to the development and globalization of the markets and also as cheap way for goods transportation because of this increment there has been growing awareness of the environmental impacts of maritime transport special on the ports or coastal regions[1]. Ship emission estimates diverge widely for all chemical compounds in both particles and gases phase and based on current hypotheses that reactive organic compounds in particle as well as in gas phase of aerosols are particularly relevant the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE)[2]. Gas phase containing different categories of organic compounds and on these categories are carbonyl compounds (CCs) which have received increased attention recently due to their important role in ground-level ozone formation and health effects [3].

A measurement campaign was conducted by the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) at the University of Rostock to investigate the characteristics of the emitted primary aerosols and their effects on lung epithelial cells. A set of state-of-the art online instrumentation measuring gases, size distribution and chemical composition were used in conjunction with the cell exposure system (Air-Liquid-Interface). Heavy Fuel Oil (HFO 180) and Distillate fuel (EN 590) were used as fuels in a one cylinder ship diesel engine operated at different loads according to ISO 8187-4 E2 for emission testing.

Our work involved sampling off CCs with two different sampling methods, commercial high sample volume DNPH cartridges and impingers almost the same as in CARB 430 method. Both sampling methods depending on derivatization with 2,4-Dinitrophenylhydrazine DNPH in acidic media. The derivatization adducts were analyzed by High Performance Liquid Chromatography with Diode Array Detector (HPLC-DAD) and by Gas Chromatography Mass Spectroscopy (GC-MS). An enhanced HPLC method was applied using a chromatography modeling software program called DryLab. The method was capable to separate and quantify 23 carbonyl compounds with correlation coefficient R^2 (0.9978) for formaldehyde till (0.9989) for decanal, the detection range for most carbonyls start from (10-1000ng) for formaldehyde and (10-500 ng) for decanal.

The GC-MS method show a good separation and detection for twenty CCs with correlation coefficient R^2 (0.9984) for formaldehyde till (0.9995) for decanal, the detection range were (0.10-15ng) for formaldehyde till (5-50ng) for decanal.

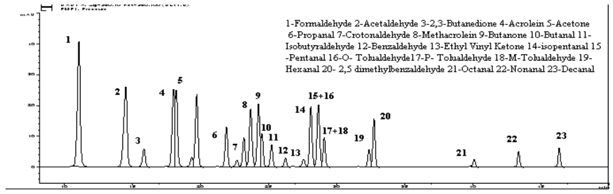

Figure (1) Separation of CCs-DNPH hydrozone by HPLC

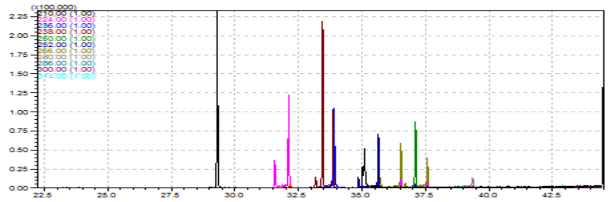

Figure (2) Separation of CCs-DNPH hydrozone by GC-MS

Real samples were collected with different sampling conditions, concerning engine loads, dilution ratios, sampling periods and fuel types. The first results for the CCs show that emissions from the heavy fuel oil usage contained more carbonyl compound than CCs from light fuel oil operation. The samples from HFO also contains a higher percentage of low molecular weight CCs with respect to the higher molecular weight CCs.

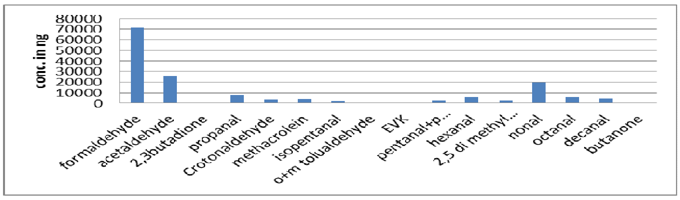

Figure (3) Carbonyl compounds in ship diesel emission (heavy fuel oil operation-HFO) given in ng/m^3

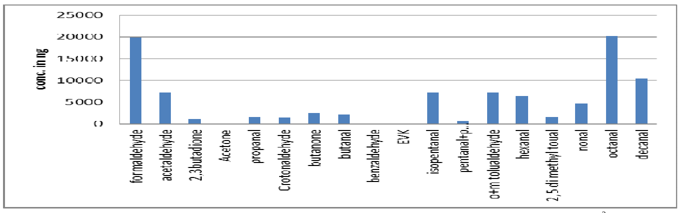

Figure (4) Carbonyl compounds in ship diesel emission (light fuel oil operation-LFO) given in ng/m^3

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