On-line and real time analysis of organic combustion products in ship diesel exhaust with mass spectrometry using various ionisation techniques

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Introduction

Diesel and heavy fuel oil exhaust emissions are a complex mixture of unburnt fuel components and partially oxidised species which are known as pollutants effecting environment and climate.

Considering the complexity of the exhaust emissions there is a requirement in having tools for detection of that fumes. For example, a proton-transfer-reaction (PTR) quadrupole-mass spectrometer (QMS) and a resonance-enhanced-multiphoton-ionisation (REMPI) time-of-flight (TOF) mass spectrometer can be a possibility for on-line and real time analysis of volatile and semi-volatile organic gas phase components, with no interfering from matrix gases. Both techniques ionise molecules in a soft way without fragmentation, so that only molecular ions are produced. PTR-MS is a chemical ionisation technique based on non dissociative proton transfer reaction between hydronium ions (H3O+) and neutral molecules like volatile organic compounds (VOCs). REMPI-TOF-MS is very sensitive and compound class selective for aromatic hydrocarbons while the PTR-QMS ionises a wide range of organic substances. The two MS are linked to the exhaust pipe of a four-stroke one cylinder research engine, which can be operated with two different fuels. Both ionisation techniques were applied to light fuel oil (LFO, diesel) and heavy fuel oil (HFO) and the results are presented here.

Method

All measurements were carried out with a four-stroke one-cylinder research engine with a nominal output of 80 kW. The engine was operated with diesel (LFO) and HFO at a nominal speed of 1500 rpm and engine loads between 25 % (20 kW) and 100 % (80 kW). The two MS were directly linked over a heated transfer line to the raw gas exhaust pipe. With the aid of an auxiliary pump a continuous flow (5 L/min) was ensured.

Results and Discussion

![Image](https://via.placeholder.com/150)

Fig. 1: Shows (A) the four-stroke one cylinder research engine; (B) the experimental setup: sampling line from exhaust pipe to REMPI-TOF-MS (setup similar to PTR-QMS).

![Image](https://via.placeholder.com/150)

Fig. 2: Shows PTR-QMS Data of (A) a mass spectrum of diesel (LFO) exhaust at engine start; (B) a comparison of an averaged diesel (LFO) and HFO exhaust mass spectrum over 10 cycles at 25 % (20 kW) load.

Compared to normal engine conditions, the exhaust emissions are much higher directly after starting the engine (Fig. 2: A and B) with dominant signals at m/z 43, 45, 57 and 59. The signal at m/z 45 belongs to acetaldehyde while the peak at m/z 59 can be assigned to different substances: on the one hand to propionaldehyde and on the other to acetone, which has normally a larger stake in the exhaust [1,2]. The aldehyde emissions in particular have consequences for air quality, because of their high reactivity towards hydroxyl radicals and their role as radical sources upon photolysis. Although PTR-MS is a soft ionisation method, some signals (e.g. m/z 43, 57, 71) are probably fragments of long-chained (C₁₅ – C₂₀) alkanes, alkenes and aldehydes of the unburnt fuel [3].

The comparison of diesel (LFO) and HFO exhaust at 25% (20 kW) load (Fig. 2, B) shows no significant differences of the main compounds.

Conclusion

Both proton-transfer-reaction MS and resonance-enhanced-multiphoton-ionisation MS are useful for on-line and real time monitoring of organic gas phase exhaust components in engine emission studies due to their high sensitivity and fast time response. The PTR method is well suited for the observation of aliphatic compounds, while the REMPI method is compound class selective to aromatic hydrocarbons.

Literature