Pyrolyses of the Halomethanes CF_3Br and CF_2ClBr in a Running Diesel Engine

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Abstract:

The feeding of a running diesel engine with the fire extinguishing agents CF_3Br (Halon 1301) and CF_2ClBr (Halon 1211) resulted in the formation of numerous halogenated organic compounds. Mass balance showed unreacted halomethanes (1211: 65 %; 1301: 45 %) and small amounts of inorganic halogenides (for fluoride based on total input: 1301: 7 %; 1211: 2,5 %). Mass spectrometry of TD-gas chromatograms lead to the identification of several volatile halogenated species.

1 Introduction

To remove the fire extinguishing agents CF_2ClBr and CF_3Br from closed engine rooms after application they are to be sucked into the running engines (approx. 1 % of the induction air).
Further to the ecotoxicological relevance of the pure gases and the toxicological importance of the pyrolysis products (1,2) reactions with the diesel gasoline are to be expected to form a number of halogenated hydrocarbons under these quasi autoclave conditions.

2 Experimental part

The construction of the engine test bed, the sampling procedures on filters and different sorbates as well as the methods for analysing the organic halogenated hydrocarbons are described elsewhere (3).
For the mass spectrometric determination, the samples, sorbed on Tenax^R, were thermodesorbed into a chrompack CP 9000 gas chromatograph with a TCT injector and analysed by a Finnigan MAT 1020 mass spectrometer.
To determine the degree of pyrolysis, the calibration was done by feeding different quantities of pure halon into the dilution channel and by taking samples in glass flasks (volume 22,18 ml) simultaneously. The contents of the vessel was exchanged approximately 20 times during the sampling procedure. 3 µl of the gas mixture were analysed gas-chromatographically. The retention time was 3,45 min for Halon 1301 and 3,70 min for Halon 1211.
Under the same analytical conditions the contents of unpyrolyzed halon was determined by feeding the mixture into the running engine. All ECD-chromatograms showed only one peak.
The halogenides F^-, Cl^- and Br^- were determined by means of ion chromatography (IC) using the ion chromatograph 2000i supplied by M/S Dionex, equipped with a pre-column AG4, a separation-column AS4A, a micro-membrane suppressor and a conductivity detector. At a pressure of 1300 psi there was a flow of 2 $ml \cdot min^{-1}$; the anions were separated at room temperature.

An aqueous solution of 0,75 mM $NaHCO_3$/2,0 mM Na_2CO_3 served as the sorption agent for inorganic halogenides and as the liquid phase. The suppressor solution for reducing the background conductivity was 0,025 N sulfuric acid.

After sampling the filter was eluted with 10 ml of mobile phase solvent. The samples and the eluates were cleaned by filtration through a Millex filter with a pore size of 0,22 μm. Apart from this processing the solutions were taken directly for the analysis.

3 Results

3.1 Degree of pyrolysis

The degree of pyrolysis was surprisingly low for both fire extinguishing agents. Under the applied conditions 45 % of the CF_3Br that had been introduced were verified in the waste gas, and 65 % of the CF_2ClBr were found. This percentage remained constant, even when different quantities were added (Tab. 1).

Table 1: Degree of pyrolysis for Halon 1211

halon flow intake air l/min	percentage halon %	halon flow waste gas l/min	degree of pyrolysis %
4,95	0,41	3,11	37,2
4,21	0,35	2,76	34,5
1,82	0,15	1,19	34,8

3.2 Determination of the inorganic halogenides

Contrary to all expectations only a small percentage of the halons was converted into hydrogene halogenides or salts.

In the case of CF_3Br, only 6,7 % of the maximum yield of fluoride were found, of which 23 % were bound to particles. The amount of bromide was below the detection limit of the IC, and consequently the conversion was below 0,5 %.

Similarly CF_2ClBr showed a very low percentage of conversion into hydrogene halogenides or their salts, when added into a running diesel engine (Tab. 2).

Table 2: Conversion of Halon 1211 into inorganic halogenides

halogenides	max. quantity (g)	measured quantity (g)	%	on Filter (g)	%	in impingers (g)	%
F^-	27,5	0,68	2,5	0,30	43,4	0,38	56,6
Cl^-	25,7	0,34	1,3	0,15	43,5	0,19	56,5
Br^-	57,9	0,82	1,4	0,78	95,3	0,04	4,7

This determination revealed a special position for bromide. Almost the total proportion of bromine compounds soluble in the eluate was retained on the filter, i.e. bound to soot particles.

3.3 New halogenated molecules

For only very low percentages of the Halons were converted into inorganic halogenides, the main products of the combustions were from transhalogenation reactions between the diesel and the fire extinguishing agents. As already reported the thermodesorption analyses (TD) and the analyses of the eluates of filters and charcoals, respectively, with either GC/ECD or GC/FID proved the formation of new halogenated molecules.

The mass spectrometry of the samples was not very sensitive compared to ECD results but more information was obtained by determining the fragments m/e 79 and 81 (Br) in case of brominated molecules. Figures 1 and 2 show the chromatograms obtained for Halon 1211 and Halon 1301 and the respective mass selective chromatograms.

Figure 1: Total ion current and mas selective GC/MS plot of Halon 1301.

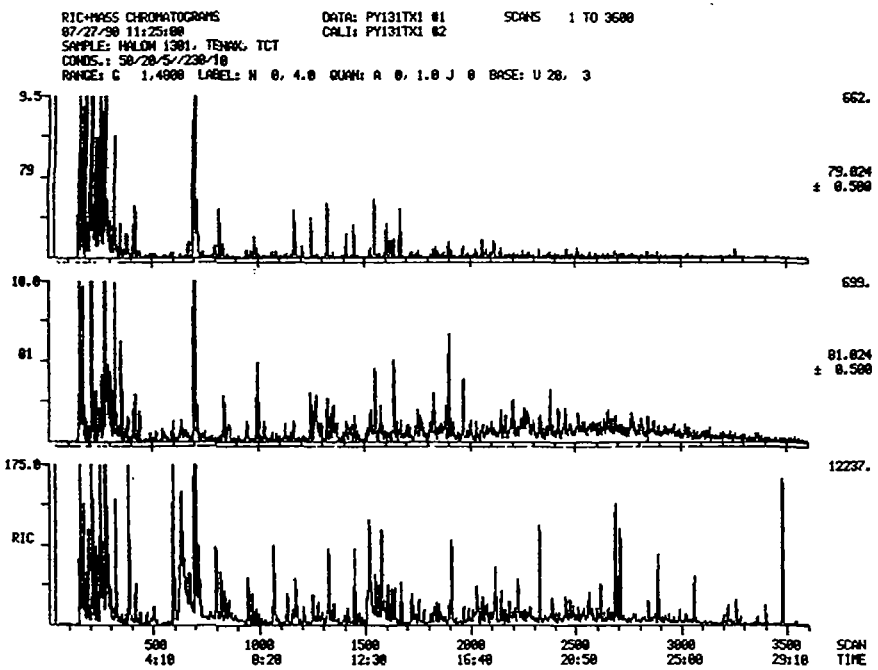
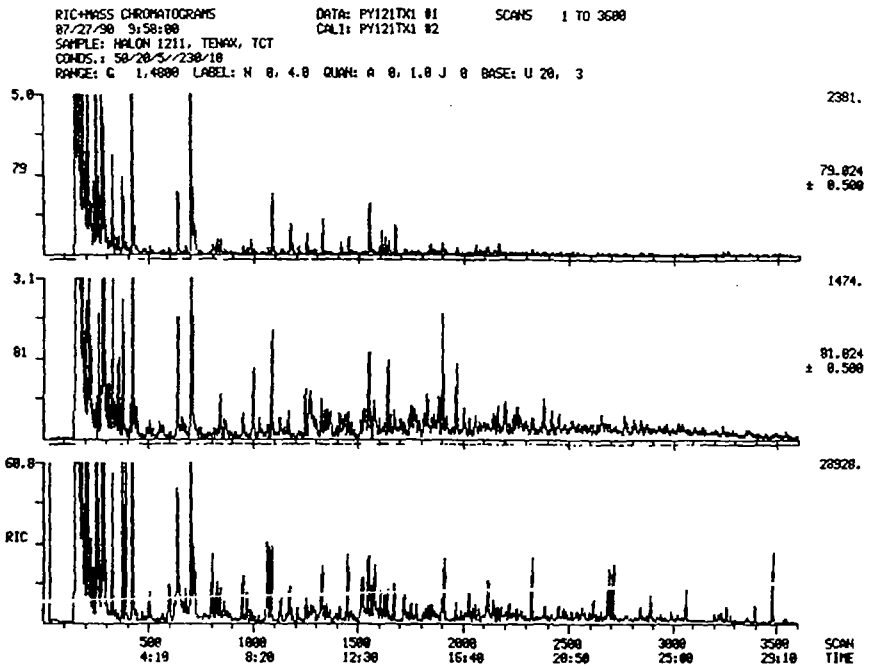


Figure 2: Total ion current and mas selective GC/MS plot of Halon 1211.



Mono- and polybrominated methanes, ethanes and propanes could be determined as well as brombenzene. As already indicated by the GC/ECD chromatograms only volatile brominated molecules could be identified by the method used. Future work will focus on possible fluorinated products of the combustion.

References

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