

Thermal breakdown of extinguishing agents

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Abstract

Four fire extinguishing agents has been investigated, bromotrifluoromethane, Halon 1301, pentafluoroethane, HFC 125, heptafluoropropane, HFC 227ea and dodecafluoro-2-methylpentane-3-one, C₆F-ketone. The inerting concentrations were determined in a cubic pressure vessel with a volume of 8 litres. A cup burner was used to find the flame-extinguishing concentrations for the agents. Thermal breakdown was also studied and for this purpose the studied agent was introduced into a flame of propane in a tubular burner. The produced combustion products were analysed both with conventional IR-techniques and with FTIR. It was found that HF and COF₂ were produced from all studied agents. Models and theories on the mechanisms of the breakdown processes are presented.

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SUMMARY

Until recently fluorinated, chlorinated and brominated hydrocarbons such as (CF_3Br) and (CF_2ClBr) were extensively used as fire suppression agents. Unfortunately Halons have high stratospheric ozone depletion potential and can no longer be used. It is therefore vital to find new agents which have the same good qualities without damaging the stratospheric ozone layer.

In this report results from a project funded by Brandforsk with supporting funding via the EU Large Scale Facility program and Solvay Fluor GmbH are presented. The extinguishing capability under different fire conditions has been investigated for four extinguishing agents, HFC 227ea, HFC 125, a C_6F -ketone, 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one and Halon 1301. The latter was incorporated as a reference. One important aspect was also to study and analyse the thermal break down products when the extinguishing agent is applied to a fire.

Experimental set-ups were designed in order to compare the efficiency of extinguishing agents and to determine their thermal breakdown products. Three different set-ups were used:

- 8-litre bombs were used to determine the inerting concentration.
- A cup burner where the extinguishing agent was mixed with air in varying proportions and introduced into a propane flame was used to find the extinguishing concentration.
- Thermal breakdown of the extinguishing agent was studied in an apparatus consisting of a tubular burner, where the extinguishing agent was mixed with the fuel in different ratios, in connection with a calorimeter equipment.

The inerting concentrations were determined with propane as fuel. Generally the results are in good agreement with results found in the literature. For HFC227ea the inerting concentration was 11.5 %, for HFC125 14 %, for the C_6F -ketone it was 7 % and for Halon 1301 the inerting concentration was 7.5 %.

The extinguishing concentration for the four studied extinguishing agents were determined in a cup burner with propane as fuel and the results were: for HFC 227ea the extinguishing concentration was 8 %, for HFC 125, 10 %, for the C_6F -ketone it was 6.5 % and for Halon 1301 the inerting concentration was 2 %.

In the project great effort was made to determine the thermal breakdown products when a halogenated extinguishing agent is introduced to a fire. It has also been important to try to understand the mechanisms behind the production of different products. For this purpose a number of reaction paths for the production of HF and COF_2 are presented. These compounds are well known, poisonous substances produced from fluor containing extinguishing agents.

Numerous experiments with the four extinguishing agents were performed in the tubular burner tests where the agent was introduced into a flame of propane. The breakdown products were analysed both with conventional IR technique and FTIR (Fourier Transform Infra- Red). The heat production during the experiments was also measured and it was found that HFC 125 and HFC 227ea give a rise in the heat release and that Halon 1301 gives a reduction in the RHR when added to the flame. The more recently introduced extinguishing agent, C_6F -ketone did not give any significant contribution to the RHR.

Production of HF and COF_2 was found in experiments with all four extinguishing agents. It was found that the main fraction of fluorine ends up as HF for HFC 227ea and HFC 125 at lower relative application rates. Closer to extinguishing concentrations the fraction recovered as COF_2 increases, but the total recovery of fluorine including HF is below 40 % at 90 % relative

application rate. The recoveries of fluorine as HF and COF₂ for C₆F₁₂O is lower compared to HFC 227 and HFC 125. There is a clear difference in the recovery for Halon 1301 where an almost quantitative recovery as HF or COF₂ is found for fluorine. Halon 1301 contains bromine also, which to a large part is recovered as HBr.

The yield of HF decreases for HFC 227ea, HFC 125 and C₆F₁₂O with an increased application rate of the extinguishing agent. The yield of HF is very high for both HFC 227ea and HFC 125, about 0.7 g/g at low relative application rates. The yield of HF from C₆F₁₂O is significantly lower at low relative application rates. No results are available for high relative application rates. The yield of HF from Halon 1301 is rather constant at the two relative application rates investigated, about 0.4 g/g. The yield of COF₂ instead increases with an increased application rate for all extinguishing agents. Probably, at low relative application rates the organic extinguishing agent is largely combusted and fluorine is effectively transferred to HF. At higher relative application rates, where the extinction effect becomes more evident, the combustion of the extinguishing agent is less effective and the formation of COF₂ is preferred before HF.

It can be concluded that for all the tested extinguishing agents it is important to have an application system where the amount of agent is large enough to extinguish the fire fast and to ensure that the agent is well distributed through out the fire area. If this is achieved the amount of troublesome combustion products will be minimised.

SAMMANFATTNING

Under lång tid har halogeninnehållande släckmedel, haloner, såsom (CF₃Br) and (CF₂ClBr) utgjort en stor andel av marknaden med släckmedel i de fall då inte vatten eller vatteninnehållande medel är lämpliga. Haloner har tyvärr en stor påverkan på ozonlagret och därför är de inte längre tillåtna. Därför är det viktigt att finna nya alternativ med de goda egenskaper som halonerna har men som inte påverkar ozonlagret negativt.

Ett projekt, Termisk nedbrytning av gasformiga halonersättningsmedel, har finansierats av Brandforsk med tilläggsfinansiering via EU:s program för Large Scale Facility och Solvay Fluor GmbH. Syftet med projektet var att undersöka släckförmåga för olika släckmedel under varierande brandförhållanden för några olika släckmedel. De som undersökts är: HFC 227ea, HFC 125, en C₆F-ketone, 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one och Halon 1301. Den senare har använts som referens. En mycket viktig aspekt vid användandet av släckmedel är vilka sönderdelningsprodukter som bildas när släckmedlet används för släckning av en brand.

Tre olika typer av experiment utfördes för att kunna jämföra de olika släckmedlens släckförmåga och för att kunna bestämma vilka sönderdelningsprodukter som bildas. De utrustningar som användes var:

- 8-liters tryckbehållare, bomber, användes för att bestämma inerteringsgränser för släckmedlen.
- För att bestämma släckkoncentrationen för de olika släckmedlen användes en s.k. cup burner där varierande koncentrationer av släckmedlet blandas med luft och därefter förs in i en propanflamma. Mängden släckmedel ökas tills flammen släcks.
- För att bestämma vilka sönderdelningsprodukter som kan bildas när släckmedlet förs in i en flamma användes en rörbrännare tillsammans med en konkalorimeterutrustning.

Vid bestämningen av inerteringsgränserna användes propan som bränsle. Resultaten är generellt i bra överensstämmelse med värden som anges i litteraturen. För HFC 227ea var inerteringsgränsen 11.5 %, för HFC 125 14 %, för C₆F-ketonen var den 7 % och för Halon 1301, 7.5 %.

Släckkoncentrationerna för de fyra studerade släckmedlen bestämdes i en cup burner med propan som bränsle och resultaten var: för HFC 227ea var släckkoncentrationen 8 %, för HFC 125, 10 %, för C₆F-ketonen var den 6.5 % och för Halon 1301 var släckkoncentrationen 2 %.

Stor möda lades ner i projektet för att bestämma de sönderdelningsprodukter som bildas när ett halogeninnehållande släckmedel förs in i en flamma. En viktig del har också varit att försöka förstå de mekanismer som styr bildandet av olika föreningar. I rapporten presenteras därför att antal möjliga reaktionsvägar för bildandet av HF och COF₂. Dess fluorföreningar är viktiga kända, giftiga produkter som bildas vid användandet av fluorinnehållande släckmedel.

Ett stort antal försök genomfördes för att bestämma sönderdelningsprodukterna vilka analyserades dels med konventionell IR-teknik men även med FTIR (Fourier Transform Infra-Red). Effektutvecklingen under försöken mättes också och resultatet blev att HFC 125 och HFC 227ea gav en ökad värmeutveckling när de förs in i en flamma. Halon 1301 däremot ger en sänkning av effektutvecklingen. Det nyare släckmedlet, C₆F-ketonen, hade inte någon märkbar påverkan på effektutvecklingen.

HF och COF₂ producerades vid försök med samtliga släckmedel. För HFC 227ea och HFC 125 återfinns den största andelen fluor som HF vid låga relativa påföringshastigheter. Närmre

släckkoncentrationen ökar andelen COF_2 men den totala återvinningen av fluor inklusive det som återfinns som HF är under 40 % vid 90 % relativ påföringshastighet. För $\text{C}_6\text{F}_{12}\text{O}$ är återvinningen av fluor som HF och COF_2 lägre än för HFC 227ea och HFC 125. Det är en markant skillnad mot Halon 1301 där en närmast total återvinning av fluor som HF och COF_2 kan erhållas. Halon 1301 innehåller även brom och detta återfinns till stor del som HBr.

Utbytet av HF minskar för HFC 227ea, HFC 125 och $\text{C}_6\text{F}_{12}\text{O}$ med ökande påföringsmängd. Både för HFC 227ea och HFC 125 är utbytet av HF högt, omkring 0.7 g HF/g släckmedel vid låga påföringshastigheter. Utbytet av HF från $\text{C}_6\text{F}_{12}\text{O}$ är betydligt lägre vid låga relativa påföringshastigheter. För höga påföringshastigheter finns inga tillgängliga resultat. För Halon 1301 är utbytet av HF ganska konstant, 0.4 g/g för de två påföringshastigheter som har undersökts. För samtliga undersökta släckmedel ökar produktionen av COF_2 med ökande påföringshastighet. Vid låga relativa påföringshastigheter är det troligen så att de organiska släckmedlen till stor del förbränns och fluor därmed effektivt överförs till HF. Vid högre relativa påföringshastigheter, där släckeffekten blir mer påtaglig, blir förbränningen av släckmedlet mindre effektiv och bildandet av COF_2 gynnas på bekostnad av bildandet av HF:

Av de genomförda försöken kan slutsatsen dras att för samtliga testade släckmedel är det av stor vikt att ha ett påföringssystem där mängden släckmedel är tillräckligt stor för att snabbt släcka branden och det är även viktigt att släckmedlet kan fördelas väl över hela brandytan. Om detta kan uppnås minskas produktionen av besvärliga förbrännings- och sönderdelningsprodukter.

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1 INTRODUCTION

Until recently fluorinated, chlorinated and brominated hydrocarbons such as CF_3Br and CF_2ClBr were extensively used as fire suppression agents. Unfortunately Halons have high stratospheric ozone depletion potential and can no longer be used. It is therefore vital to find new agents which have the same good qualities; substances which are easy to produce, store and transport – effective extinguishing agents which are not harmful to the humans who use them – the substances must not damage the materials around the fire, this is very important in e.g. aircrafts, computer systems and libraries. Extensive research is conducted on alternative agents that have these good properties without damaging the stratospheric ozone layer.

Different approaches have been used to find new systems for fire extinguishment for example:

- Water mist
- Inert gases
- Aerosols and powders
- Pressure condensed gases

Among these the pressure condensed gases are those which have properties most similar to the Halons. Many of these new agents contain F and can produce hydrogen fluoride, HF and other fluorinated compounds when in contact with flames. HF is dangerous to humans [1] so this potential problem must be studied and understood before introducing new agents on the market.

A project funded by Brandforsk with supporting funding via the EU Large Scale Facility program and Solvay Fluor GmbH was initiated in order to investigate the potential of new chemical compounds as fire extinguishing agents. The goal is to measure its extinguishing capability under different fire conditions as well as to analyse thermal breakdown products in order to estimate possible application areas for the chemical compound as a Halon replacement agent and effects of the thermal breakdown products on humans, environment and materials. The project has both experimental and theoretical parts.

2 THEORETICAL BACKGROUND

Fire extinguishing agents are combustible and they thermally decompose at elevated temperatures. The flammability limits are higher with respect to ordinary fuels. However, the decomposition of fire extinguishing agents leads to the formation of toxic compounds such as HF. In order to understand and predict the concentration of toxic species when introducing fire suppressing agents into the combustion process, extinguishing mechanisms and the paths of formation of toxic species, chemical mechanisms need to be developed and applied in combustion models.

The development of prediction tools describing the formation of species in fires where extinguishing agents are involved can be divided into different steps.

- At first there is the development of a chemical reaction scheme involving all species relevant to the process.
- Then a combustion model needs to be applied to solve the Navier-Stokes equations for the reactions. The application of a combustion model is necessary for the determination of concentration of toxic species in the fire.
- The transport of the species in the fire is to be solved by applying a CFD code, which helps defining the distribution of toxic gasses in the enclosure or the space. This is essential for risk assessment.

As computation time gets more and more available, the combustion society has slowly begun to consider modelling the kinetics of fires including extinguishing agents. The theoretical part of the project is a pilot study on the achievements in this field considering different fire extinguishing agents. It gives a survey on the different research related to the effect of fire retardants in combustion processes.

A number of experimental and theoretical studies on chemical mechanisms describing fire extinguishing agents can be found in literature. Only very few studies modelling the combustion process, have yet been performed. This survey will focus on investigations considered relevant for implementation into models in order to give a complement to the experimental study performed in the project.

The current study involves the thermal decomposition of the three replacement agents for Halon 1301 (CF_3Br), namely HFC227ea ($\text{CF}_3\text{-CHF-CF}_3$), HFC125 ($\text{CF}_3\text{-CHF}_2$) and a C_6F -ketone, 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one with the structure ($\text{CF}_3\text{CF}_2\text{C(O)CF(CF}_3)_2$). The measurements undertaken involve mixing and combustion of one of the above mentioned agents and a fuel. The fuel applied is propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) and for calibration purposes, heptane (C_7H_{16}).

Most existing studies focus on the fire retarding and extinguishing characteristics of the agents [2]. One experimental study on thermal decompositions of mixtures of fuel and extinguishing agents has been found [3]. In his thesis Ditch looked into the emission of HF.

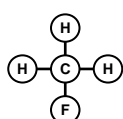
This section will start out by presenting the chemical mechanisms on fire extinguishing agents in literature. It will also mention appropriate chemical mechanisms for the fuel involved in the experiments, propane. Finally suggestions on the combustion model including modelling of the turbulence will be given.

2.1 Chemical mechanisms

The first step of modelling the thermal decomposition of gaseous fire extinguishing agents is the development of chemical reaction schemes of the gaseous species and the fuel. This section will give a state of the art on existing mechanisms. At first mechanisms on fluorinated agents will be discussed followed by the reference agent – Halon 1301 and other alternatives. The mechanisms present a necessary input for combustion models. They also indicate the domains where certain species are preferably formed. The focus of this work is on toxic substances measured in the experimental part.

2.1.1 Fluorinated extinguishing agents

One of the most detailed chemical mechanisms, as well as a list of thermochemical data can be found in Burgess et al. [4]. The mechanism is formed in analogy to hydrocarbon mechanisms, which are well known [5]. With respect to the structure of hydrocarbon mechanisms one or more hydrogen atoms are replaced with fluorine as is indicated in the structure below.

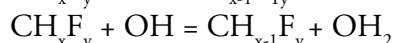
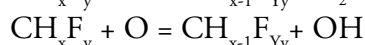
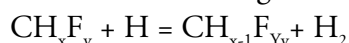


Reaction classes are described beginning with C_1 fluorinated hydrocarbon chemistry involving species with one carbon atom up to C_2 . Fluor reactions are introduced in addition to the H/C/O reactions, which can be found in literature and which will be described in a following section. Toxic species of special interest are HF and COF_2 .

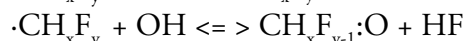
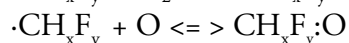
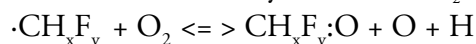
Formation of hydrogen fluoride

Different paths of the hydrogen fluoride, HF, formation have been measured at different temperatures (consult [4] for further references). However, Burgess et al. in [4] present and validate a sum of reaction schemes developed by different researchers. The mechanism accounts for reactions with fluoromethanes (CH_3F , CH_2F_2 , CHF_3 , CF_4), fluoromethyl radicals ($\cdot CH_2F$, $\cdot CHF_2$, $\cdot CF_3$) and fluoromethylenes and fluoromethylidyne radicals ($:CF_2$ and $:CHF$) as well as carbonyl fluorides and fluoromethoxy radicals ($CHF=O$, $CF_2=O$ and $\cdot CF=O$). In their C_1 -chemistry, Burgess and co-workers consider 14 species. A number of minor insensitive species involved in the reactions were neglected.

1. H abstraction through reaction mainly with H, O, OH and other species:



2. Fluoromethane metathesis reactions with methyl, ethyl, vinyl and fluoromethyl radicals.
3. Formation of carbonyl fluorides $CF_2=O$ through:



4. Destruction of carbonyl fluorides through hydrogen abstraction and addition reactions as well as OH abstraction.

The C_2 -mechanism includes 34 species and 450 reactions.

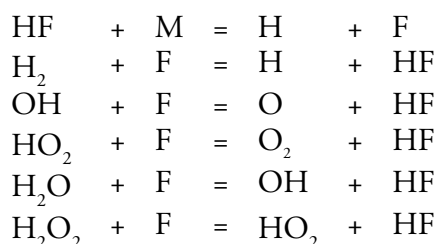
The following research results are based on data and the summary from the work by Burgess and co-workers [4]. Documentation can be found for the reference agent Halon 1301 and agent HFC227ea and will be discussed in the following subsections. Reaction schemes for other agents

will also be introduced. Finally suggestions will be made how to model the three missing agents and chemical mechanisms applicable for the two fuels will be presented.

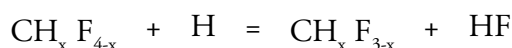
Since our experimental study focuses on the formation of HF, we will now take a look into the formation and decomposition of this toxic species. Initially in Burgess' mechanism HF is formed in the following groups of reactions.

C1 chemistry:

- H/F/O chemistry with the following reactions:



- The next group of reactions responsible for the formation of HF is the F abstraction by hydrogen atoms from fluoromethanes, C1 reactions of the character:

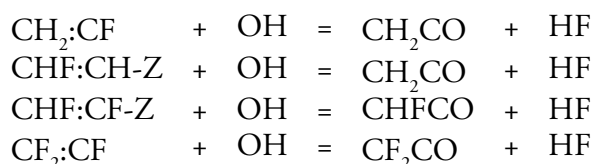


Where $x \in \{0,4\}$

- The species also occurs in the H abstraction of fluoromethanes from HCO by fluoromethyls as CH_2F , CHF_2 and CF_3 .
- The oxidation of the same fluoromethyls by OH and the oxidation of the fluoromethylenes CHF and CF_2 by OH and H_2O ,
- The destruction of the same fluoromethylenes by H, CH_2O and CF_2 .

C2 chemistry:

- Thermal decomposition of fluoroethanes ($\text{CH}_3\text{-CH}_2\text{F}$, $\text{CH}_3\text{-CHF}_2$, $\text{CH}_3\text{-CF}_3$, $\text{CH}_2\text{F-CH}_2\text{F}$, $\text{CH}_2\text{F-CF}_3$, $\text{CHF}_2\text{-CHF}_2$ and $\text{CHF}_2\text{-CF}_3$).
- A series of reactions leading to the formation of HF is the insertion of fluoromethanes by reaction with CH_2 (singlet), CHF and CF_2 ,
- the association of fluoroethyls with O_2 , O and OH
- and the thermal decomposition of fluoroethylenes, requiring high activation energies:
 - activated decomposition of fluoroethylenes by HF elimination
 - activated decomposition of fluoroethylenes by vinyl+H where HF is eliminated
- Oxidation of fluorovinyles by OH, expressed by the following four reactions:



- Reactions with F lead most probably to the formation of HF.

However, the mechanism by Burgess et al. includes 134 reactions involving HF species. The formation ranges from low activation energies to energies of the order of e^{16} . As mentioned before the mechanism goes up to C2 and presents a solid base for further studies.

Carbonyl fluoride, COF₂

COF₂ occurs in the following 24 reactions of the total scheme, Table 1.

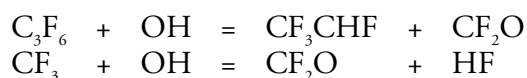
Table 1: Reaction path involving COF₂ (Burgess, 1996) [4].

	A ¹	b	E ²
1. CHF ₂ + O ₂ = COF ₂ + O + H	2.260E+09	1.14	69.0822
2. CHF ₂ + O = COF ₂ + H	3.700E+13	0.0	0.0
3. CF ₃ + O = COF ₂ + F	1.870E+13	0.0	0.0
4. CF ₃ + OH = COF ₂ + HF	2.000E+13	0.0	0.0
5. CHF ₂ + HO ₂ = COF ₂ + OH + H	1.500E+13	0.0	0.0
6. CF ₃ O + H = COF ₂ + HF	1.000E+14	0.0	0.0
7. CF ₃ O + H ₂ = COF ₂ + HF + H	1.000E+13	0.0	20.934
8. CF ₃ O + H ₂ O = COF ₂ + HF + OH	1.000E+13	0.0	20.934
9. CF ₃ O + CH ₄ = COF ₂ + HF + CH ₃	8.000E+12	0.0	9.62964
10. CF ₃ O + C ₂ H ₆ = COF ₂ + HF + C ₂ H ₅	1.200E+13	0.0	9.62964
11. CF ₃ O + C ₂ H ₄ = COF ₂ + HF + C ₂ H ₃	1.000E+13	0.0	20.934
12. CF ₃ O + C ₂ H ₂ = COF ₂ + CH ₂ CF	1.000E+13	0.0	20.934
13. CF ₃ O + CH ₂ O = COF ₂ + HF + HCO	5.000E+12	0.0	20.934
14. CF ₃ O + HCO = COF ₂ + HF + CO	5.000E+12	0.0	8.3736
15. CF ₂ + O ₂ = COF ₂ + O	2.000E+13	0.0	110.9502
16. CF ₂ + OH = COF ₂ + H	2.000E+13	0.0	14.6538
17. CF ₂ + HO ₂ = COF ₂ + OH	1.000E+13	0.0	14.6538
18. CFO + F = COF ₂	1.000E+12	0.0	0.0
19. COF ₂ + H = CFO + HF	2.400E+07	1.88	150.30612
20. COF ₂ + H = CFO + HF	1.200E+10	0.83	93.36564
21. COF ₂ + H = CFO + HF	5.500E+08	1.42	79.13052
22. CF ₂ O + H ₂ O = CO ₂ + HF + HF	7.400E+3	3.84	105.08868
23. COF ₂ + OH = CO ₂ + F + HF	2.700E+03	2.38	87.9228
24. CFO + CFO = CO + COF ₂	2.230E+13	0.0	1.3314024

In this mechanism COF₂ is a product in reactions with reactant CF₃O and other hydrocarbons. It mainly decomposes to HF.

HFC227ea, CF₃-CHF-CF₃:

Hynes et al. [6] studied the composition of the post-flame gases of a lean hydrogen-air flame doped with 1.0 mol % of the popular Halon replacement agent CF₃-CHF-CF₃. Figure 1 taken from [6] shows the post flame species concentration profiles, in particular the profile of COF₂ of a lean hydrogen-air flame inhibited by 1.0 mol % agent as a function of Φ , the equivalence ratio, formed by the reaction of OH with C₃F₆ and CF₃.



¹ [kJ/mol]

² E [kJ/mol]

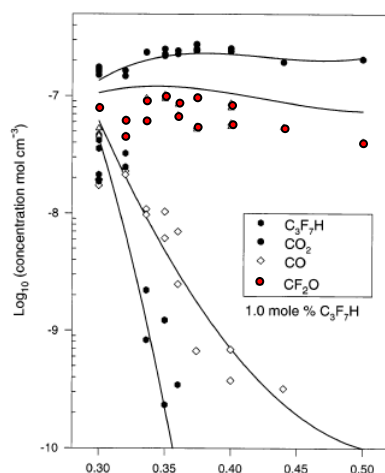


Figure 1: Post flame species concentration profiles of a hydrogen-air flame inhibited by 1.0 mol % agent as a function of Φ . The profile of COF_2 is marked with (\bullet), from [6].

In 1999 Hynes et al [7] developed a mechanism for $\text{CF}_3\text{-CHF-CF}_3$. Since COF_2 was found only in the reaction with lean mixtures and an analysis of the FTIR spectra did not reveal any trace of COF_2 for other equivalence ratios, the formation of COF_2 was neglected.

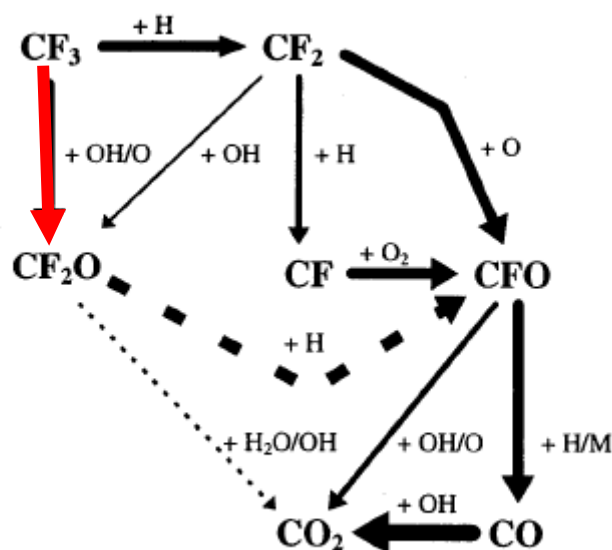


Figure 2: Reaction path. Formation of COF_2 is marked in red and the slow dissociation is marked with dash [6].

The study is an extension up to C_3 of the mechanism by Burgess and co-workers with additional 68 reactions. The experiments for validation were performed in a shocktube over a temperature range of 1200-1500K. The identification of different species was performed with GC- and FTIR-measurements and the following unknown fluorinated products were found: C_2F_6 , $\text{CF}_2=\text{CHF}$, C_2F_4 , C_3F_6 , $\text{C-C}_2\text{F}_6$, and $\text{CF}_3\text{CHFCF}_2\text{H}$. The thermodynamical data is from [4].

The increase in HF concentration with height over the burner in the lean hydrogen-air flame with 1 mole % agent can be seen in Figure 3.

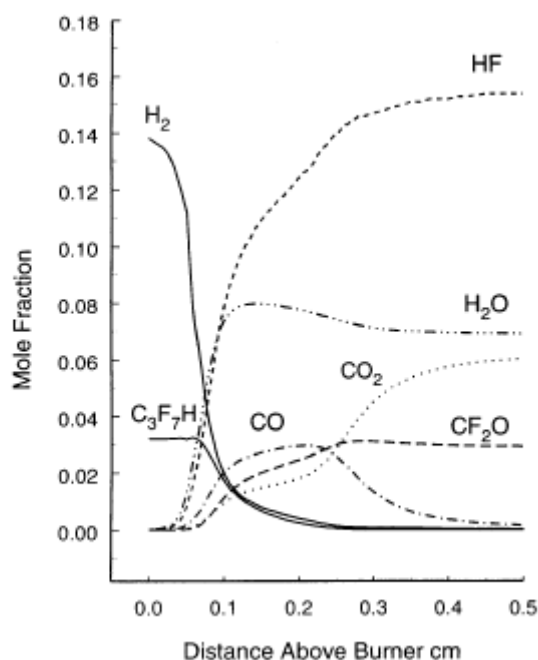


Figure 3: Profile of species of a hydrogen-air flame inhibited by 1.0 mol % agent as a function of distance above the burner in cm [6].

Two initiation paths lead to the formation of HF as shown in Figure 4.

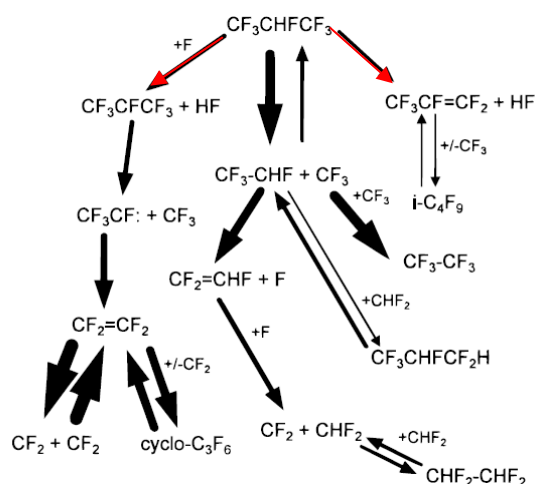


Figure 4: Reaction path. The formation of COF_2 is marked in red and the slow dissociation is marked with dash [7].

Studies on CF_3H

Linteris [8] performed experiments on chemical kinetics with a premixed bunsen-type conical hydrogen flame. The study focusses on the fire extinguishing effect of the agent. Linteris reports on the change in burning velocity and the profile of some species such as CO , CO_2 , H_2O , H_2 and O_2 as well as CF_3H . The reaction paths can be seen in Figure 5. The scheme includes 31 reactions where HF is formed in 13 reactions in a range of an A-factor of 10^7 - 10^{24} $\text{cm}^3/\text{mol}\cdot\text{s}$ and activation

energies within a range of 0-10⁴ kJ/mol. HF is formed in a number of dominant pathways, in initiation and termination reactions.

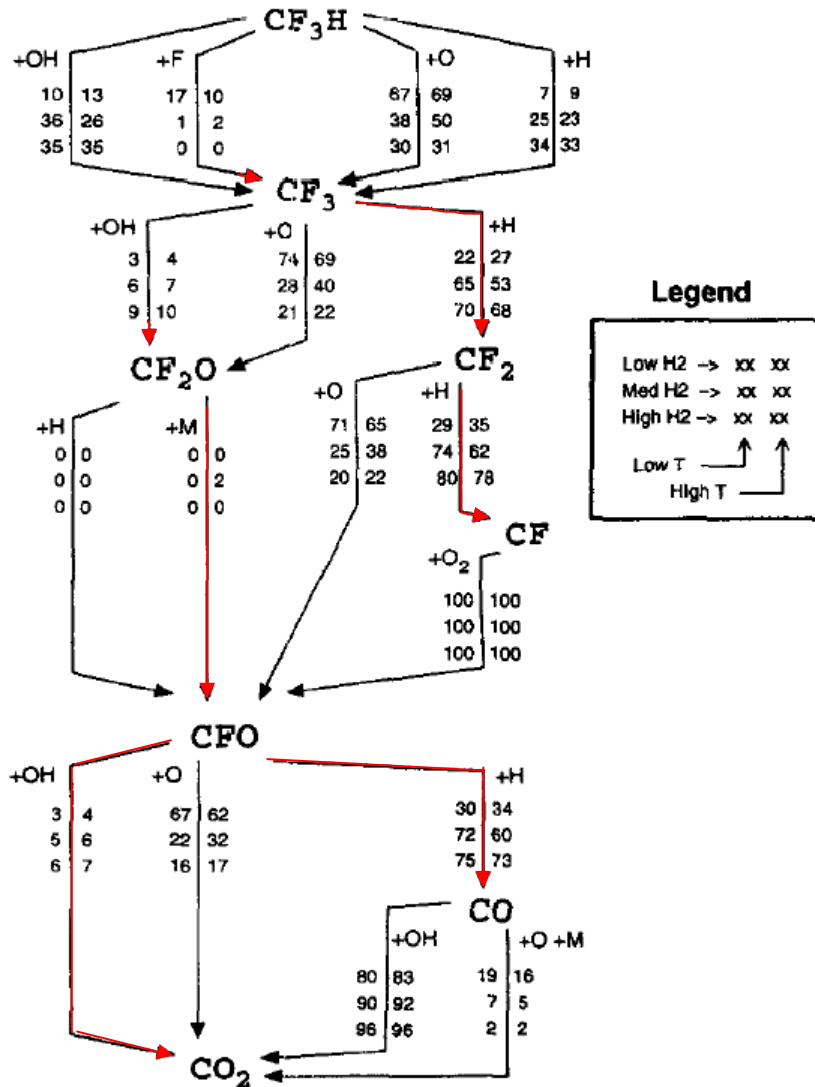
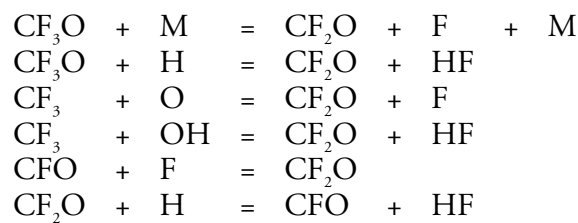


Figure 5: Dominant reaction pathways for decomposition of CF₃H in a stoichiometric premixed H₂, O₂, Ar, CO flame. The paths where HF is formed are marked with red [8].

COF₂ is involved in the following 6 reactions:



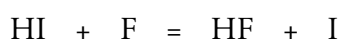
Here COF₂ is generated in reaction with CF₃O, CFO and CF₃.

HALON 1301, CF₃I and CF₃H in methane

Halogenated hydrocarbons or Halons are agents where fluorine, chlorine, bromine or iodine replaces one or more hydrogen atoms in a hydrocarbon molecule. However, Halon commonly only comprehends species containing chlorine or bromine. We adopt this latter definition. This section will deal with the mechanisms for the reference agent Halon 1301.

Babushock et al. [9] studied the mechanism of three fire retardent agents in methane/air combustion in a plug flow reactor. The mechanism of these species are documented and validated. The reaction time is found to be a function of the active radicals H, OH, and O, that are formed during the process. The investigation shows that the concentration of these species decreases with an increased addition of the agents in the flame. The thermodynamic data is from Burgess et al. [4,10]. The reaction scheme for bromine and iodine containing species includes 106 reactions and HF is formed through one path with bromine and one in reaction with hydrogen iodine.

Battin-Leclerc et al. [11] showed that CF₃I is as efficient fire inhibiting agent as Halon 1301. The study was performed on methane/oxygen combustion in a jet-stirred reactor. The paper documents modelling results applying a mechanism containing 26 species. HF is formed in one reaction :



2.1.2 Fuels

In fires the suppression agents react with the fuel. Therefore the chemical reactions of the fuel have to be considered as well. Fires involve complex multi fuels. However, single fuels are often applied to differentiate the single mechanisms.

In a work of 2000 Babushok and Tsang [12] investigated whether or not to use a single fuel such as n-heptane for the simulation of fire suppression. The reactions which were tested with the fuels methane, ethane, butane and heptane carried an uncertainty in their contribution to reactions involving the parent fuel. The suppressing mechanism is found to be similar for the tested alkane fuels. The agents suppress the concentration of radicals in the reaction with all of the tested fuels. The emission of toxic species in the reaction with fuels is studied using single fuels.

The description of single fuels can be found in many textbooks on combustion e.g. Warnatz et al. [13]. Many chemical reactions are involved even when simple fuels such as propane and heptane take part in the combustion processes. This section contains a description of one possible composition of reactions up to the formation of cyclic polyaromatic hydrocarbons via benzene C₆H₆ and phenyl C-C₅H₆. The mechanisms are based on the H₂/O₂-chemistry by Warnatz reported in Baulch et al. [5]. It includes C₁-C₄ mechanism as well as the formation of H₂-CO and oxidation via O₂ and OH. The kinetic by Warnatz is valid for lean combustion conditions. It was adjusted to rich combustion conditions by Frenklach [14].

Oxidation via O₂ and OH is responsible for the reduction of the hydrocarbons. Since flame velocities and species profiles are affected by these processes it is important to include a detailed description of the oxidation of higher order hydrocarbons. Slagle et al. [15], Warnatz [13] and Westmoreland [16] studied these processes.

2.1.3 Modelling the combustion process

Different combustion models can be applied in order to model the chemistry of fire. Such models are a necessity when the species concentration is to be determined. There are a range of models available, such as:

- Flamelet models,
- different versions of the conditional moment closure and
- probability density function methods

In order to determine the distribution in an enclosure, these models need to be implemented or coupled to CFD-codes. There are various CFD-codes available, which are based on different assumptions. The models range from Direct Numerical Simulations, a very CPU time consuming and very detailed model, to models where some chemical input is possible and models having the main focus on the flow.

2.1.4 Conclusion

Several studies on chemical mechanisms of fire suppressing agents have been provided in this section. One main path has been identified for formation of HF when Halon 1301 is applied to a fire. The mechanisms of the Halon replacement agents, except CF_3I , show that HF is formed along the whole reaction chain, at initiation reactions, chain propagation reactions and termination reactions. The study is not sufficient to determine whether or not the application of Halon replacement agents will lead to higher emissions of HF. Here the mechanisms need to be coupled to a combustion model. However, the mechanisms indicate strongly that the release of HF is higher by the application of Halon replacement agents, than when applying Halon 1301.

The presented studies show that COF_2 is formed in reaction with most Halon replacement agents except CF_3I . The path to COF_2 originates from the oxidation of CF_3 , C_3F_6 and the reaction with CF_3O . However, the formation of COF_2 was neglected in some schemes, because of its low concentration in the post flame gasses. In fires the equivalence ratio varies. The implementation of the generated mechanisms will therefore not be a tool for the prediction of the formation of COF_2 . As mentioned above the current study is not sufficient to determine the concentration of COF_2 in the post flame gasses when Halon replacement agents are applied in flames. In order to determine this, the mechanism of Hynes [Fel! Bokmärket är inte definierat.] needs further development and the mechanism needs to be coupled to a combustion model.

3 EXPERIMENTAL METHOD

Experimental set-ups were designed in order to compare the efficiency of extinguishing agents and to determine their thermal breakdown products. Three different set-ups were used:

- 8-litre bombs were used to determine the inerting concentration.
- A cup burner where the extinguishing agent was mixed with air in varying proportions and introduced into a propane flame was used to find the extinguishing concentration.
- Thermal breakdown of the extinguishing agent was studied in an apparatus consisting of a tubular burner, where the extinguishing agent was mixed with the fuel in different ratios, in connection with calorimeter equipment.

3.1 Inerting concentrations

Inerting concentrations and flammability limits of mixtures of fuel, extinguishing media and air can be determined in various types of apparatuses where the gases are contained in a closed vessel, mixed and ignited with an electric spark. In Figure 6 a flow chart of the whole equipment is shown. In the experiments reported here a cubic pressure vessel with a volume of 8 litres was used. Fuel, extinguishing agent and air was fed into the evacuated vessel. The actual concentration inside the vessel was determined by measuring the partial pressure of the added gases. After thorough mixing of the gases with an internal fan for 10 min the mixture was allowed to reach quiescent conditions during 1 min. The switch to the capacitor was closed and the capacitor discharged. A capacitor with a capacitance of 5 μF , a potential of 11 kV, giving a stored energy of 30 J was used to ignite the gas mixture. An oscilloscope was connected to the circuit in order to check the charging of the capacitor and also to see that there was no remaining charge after the discharge of the capacitor. The vessel was placed under a hood connected to an exhaust duct in order to allow all gases to be safely evacuated from the test room. The tests were documented on video and these recordings we studied to determine the inerting concentrations for the studied extinguishing agents.

3.2 Flame-extinguishing concentrations

The effectiveness of an extinguishing agent when used to extinguish small flames can be studied in different set-ups. The cup burner method is frequently used for this purpose. The method consists essentially of a diffusion flame of a gaseous or liquid fuel which is centrally placed in a quartz tube. An air stream passes the flame and the studied extinguishing media is added to the air stream. The amount of extinguishing agent is slowly increased until the flame is extinguished. This method has been standardized by a number of organisations and companies e.g. the International Organization for Standardization, ISO, Imperial Chemical Industries, ICI, and FM Global (former Factory Mutual Research Corporation), FMRC. The apparatus used in the presented experiments has dimensions corresponding to the FMRC cup burner. The burner has a diameter of 28 mm and the chimney has a diameter of 105 mm. Propane was chosen as fuel.

In Figure 7 a flow chart is given for the equipment with flow meters. A small flow of the air/extinguishing agent mixture was drawn through an oxygen analyzer to check the concentration of agent in the air flow.

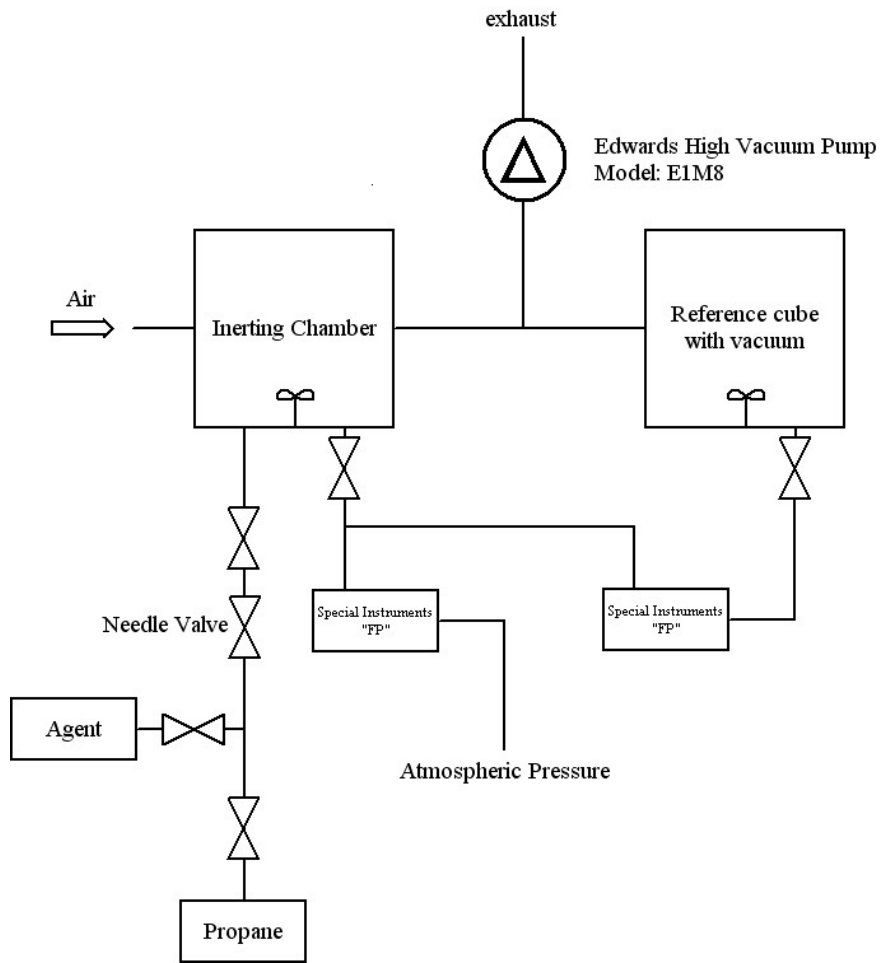


Figure 6. Flow chart of the equipment for determination of inerting concentrations.

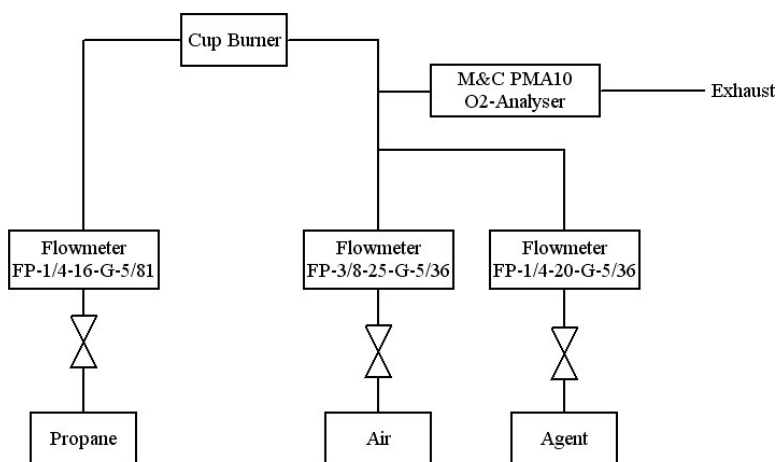


Figure 7. Flow chart of the equipment for determining flame-extinguishing concentrations.

3.3 Thermal breakdown products – Tubular burner method

In order to examine the thermal breakdown products which are produced when an extinguishing agent is applied to a fire an experimental set up was designed. Essentially it consisted of a tubular burner of the McKenna type, Figure 8, where the fuel, propane, was mixed with the extinguishing agent. The burner was cooled with water of about 10°C when a gaseous agent was used. For the experiments with liquid agent the “cooling” water had a temperature of about 40°C in order to ensure vaporisation of the agent. The burner was placed under the hood of a standard ISO 5660-1 cone calorimeter. The cone shaped radiant heater was disassembled and the remaining parts of the calorimeter were used for collecting combustion products, gas analysis and smoke measurements. The experimental set-up is shown in Figure 9. A flow chart of the set up is presented in Figure 10. The volume flow of gases through the exhaust pipe was around 20 l/s in all experiments. The flow was determined by measuring the pressure drop over an orifice plate and the smoke production was measured in the exhaust pipe. The production of combustion gases was measured on-line. Oxygen, carbon monoxide and carbon dioxide were measured with conventional techniques. Specifications for the measuring equipment are given in Table 2.

Other combustion products such as hydrogen fluoride, HF, carbonyl fluoride, COF₂, and hydrogen bromide, HBr, were analyzed with Fourier Transform Infra-Red technique, FTIR. Samples for analysis of HF content, with ion chromatography, were also intermittently taken from the exhaust pipe. Further samples were taken on activated carbon sampling tubes in selected tests for subsequent GC-MS analysis of organic combustion products. Between 100 ml and 500 ml smoke gases were sampled on each sampling tube. Several samples were taken in each test.

Table 2. Specification of instruments used for gas analysis.

Measurement	Equipment	Range, accuracy	Calibration gas
O ₂	M&C Type PMA 10, paramagnetic	0-100 volume %, ± 0.1 volume %	21 %; 9.94 ± 0.200 %
CO	Leybold-Hereaus, Binos	0-1vol % ± 1 % of full scale	0.202 ± 0.0040 ppm 202 ± 4.04 ppm
CO ₂	Leybold-Hereaus, Binos	0-20vol % ± 1 % of full scale	4.99 ± 0.0998 % 0.502 ± 0.010 %
HF, COF ₂ , HBr, etc.	FTIR, BOMEM MB-100	See text	See text

Gas flows were measured with calibrated, variable area flow meters from Fischer & Porter as indicated in Figure 10. The flow of the liquid extinguishing agent was measured with a pump, 2150 HPLC from LKB which was calibrated for the used agent.

The instrumentation used for the FTIR measurements consisted of a FTIR spectrometer (Bomem MB-100) with a multi-pass gas cell (Infrared Analysis M-38H-NK-AU). The FTIR spectrometer was used with a spectral resolution of 4 cm⁻¹. The information obtained was in the wavenumber range between 4500 cm⁻¹ and 400 cm⁻¹ and was stored in three consecutive scans which were co-added to produce a new averaged spectrum every fifteenth second. A DTGS (deuterated triglycide sulphate) pyroelectric detector was used to measure the infrared beam after passing the cell. The gas cell, which had a volume of 0.922 dm³ and a path-length of 4.8 m, was heated by a cylindrical heating element to maintain a constant temperature of 150°C. The smoke gases were continuously drawn to the FTIR with a sampling rate of 4 l min⁻¹ using a probe with a cylindrical ceramic filter (M&C 2 µm) mounted in the exhaust duct of the cone calorimeter. Both the filter and the gas sampling line (4 mm i.d. PTFE) were heated to 180°C. The FTIR was quantitatively

calibrated for: hydrogen fluoride (HF) in the concentration range 0 – 1000 ppm, carbonyl fluoride (COF₂) in the range 0 – 1085 ppm, and hydrogen bromide (HBr) in the range 0 – 1000 ppm. The FTIR was further quantitatively calibrated for e.g. CO₂, CO and HCl.



Figure 8. The McKenna burner with propane flame under the hood of the cone calorimeter.



Figure 9. The experimental set-up used when measuring thermal breakdown of extinguishing agents.

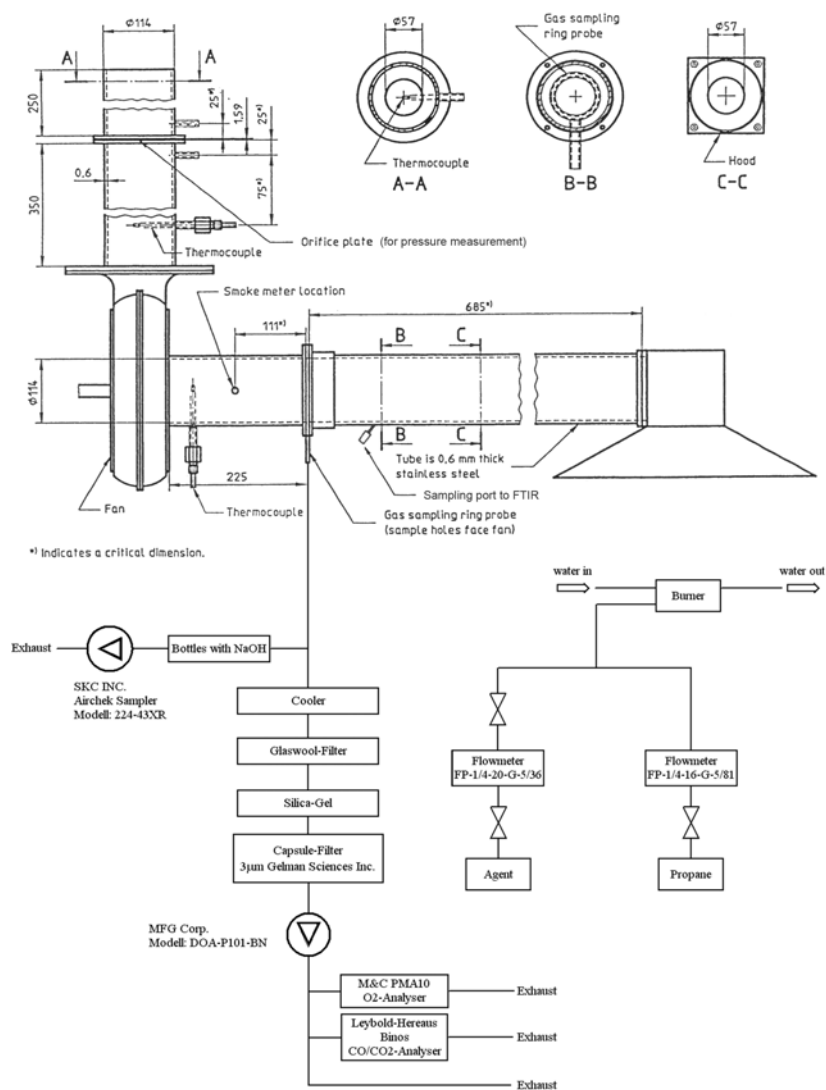

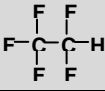
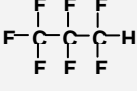
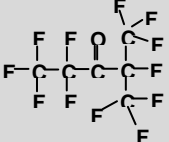


Figure 10. Flow chart of the experimental set up for the experiments for determination of thermal breakdown products from extinguishing agents.

4 EXPERIMENTAL RESULTS

Tests were performed with four different extinguishing agents: Bromotrifluoromethane, Halon 1301, pentafluoroethane, HFC 125, heptafluoropropane, HFC 227ea and dodecafluoro-2-methylpentane-3-one, C₆F₁₂O. Halon 1301 was incorporated as a reference substance since much work has been done and is published with this substance. The chemical and structural formulas and some selected physical characteristics for the agents are given in Table 3.

Table 3. Chemical and structural formulas and some characteristic physical data for the tested substances.

Substance	Chemical formula	Chemical structure	Molecular weight	Boiling point at 1 atm [°C]	Vapour pressure at 20°C [bar]	Vapour density at 20°C, 1 atm [kg/m ³]
Bromotrifluoromethane Halon 1301	CF ₃ Br		149	-58.0	14.3	6.25
Pentafluoro-ethane HFC 125	C ₂ HF ₅		120	-48.1	12.1	5.074
Heptafluoro-propane HFC 227ea	C ₃ HF ₇		170	-16.5	3.9	7.283
Dodecafluoro-2-methyl-pentane-3-one C ₆ F ₁₂ O	C ₆ F ₁₂ O		316	49.2	2.3	13.912

4.1 Inerting concentrations

Inerting concentrations were determined for the four studied extinguishing agents. Propane was used as fuel in all experiments and for each extinguishing agent the concentration of the agent was varied until the concentration was found where no ignition could be observed. The tested concentrations are presented in Table 4. Experiments were performed until the inerting concentration of the tested extinguishing agent was found. Generally the results are in good agreement with results found in the literature. Results from the presented test series and literature values of inerting concentrations are given in Table 5 and Figure 11.

Table 4 Experiments performed in 8-litres bombs.

Extinguishing agent	Test no.	Vol. % fuel	Vol. % agent	Ignition +/- No ignition -
CF₃Br	1C	3.99	7.28	+
- " -	2C	3.97	6.30	+
- " -	3C	3.98	8.28	-
- " -	4C	3.98	7.87	+
- " -	5C	3.98	7.55	+
- " -	6C	5.96	7.44	+
- " -	7C	5.96	7.74	+
- " -	8C	5.96	7.93	-
- " -	9C	2.58	4.14	-
C₂HF₅	1B	3.02	13.10	-
- " -	2B	2.52	12.08	-
- " -	3B	2.60	11.27	-
- " -	4B	2.60	10.79	-
- " -	5B	2.62	10.29	-
- " -	6B	4.20	10.44	+
- " -	7B	4.05	11.48	+
- " -	8B	4.00	12.51	+
- " -	9B	3.98	13.55	+
- " -	10B	4.01	14.60	+
- " -	11B	4.03	15.65	-
- " -	12B	4.00	15.14	-
- " -	13B	4.20	15.15	-
- " -	14B	4.22	14.63	+
C₃HF₇	1	1.97	6.43	+
- " -	2	2.56	11.12	+
- " -	3	2.57	11.17	-
- " -	6	2.57	11.20	-
- " -	7	2.63	11.64	-
C₆F₁₂O	1A	2.57	7.12	-
- " -	2A	2.59	6.10	-
- " -	3A	3.89	6.19	+
- " -	4A	3.89	6.70	+
- " -	5A	3.86	6.94	+
- " -	6A	3.91	7.14	-
- " -	7A	4.10	6.67	+
- " -	8A	4.13	6.88	+
- " -	9A	3.79	6.66	-
- " -	10A	3.72	6.85	-
- " -	11A	4.14	6.35	+
- " -	12A	4.11	6.15	+

Table 5. Inerting concentration for extinguishing agents

Extinguishing agent	Inerting concentration from test [%]	Inerting concentration from literature [%]
CF₃Br	7.5	8.3-8.7 ¹⁷
C₂HF₅	14	15.5-16 ¹⁷
C₃HF₇	11.5	11.6 ¹⁸
C₆F₁₂O	7	8-9 ¹⁹

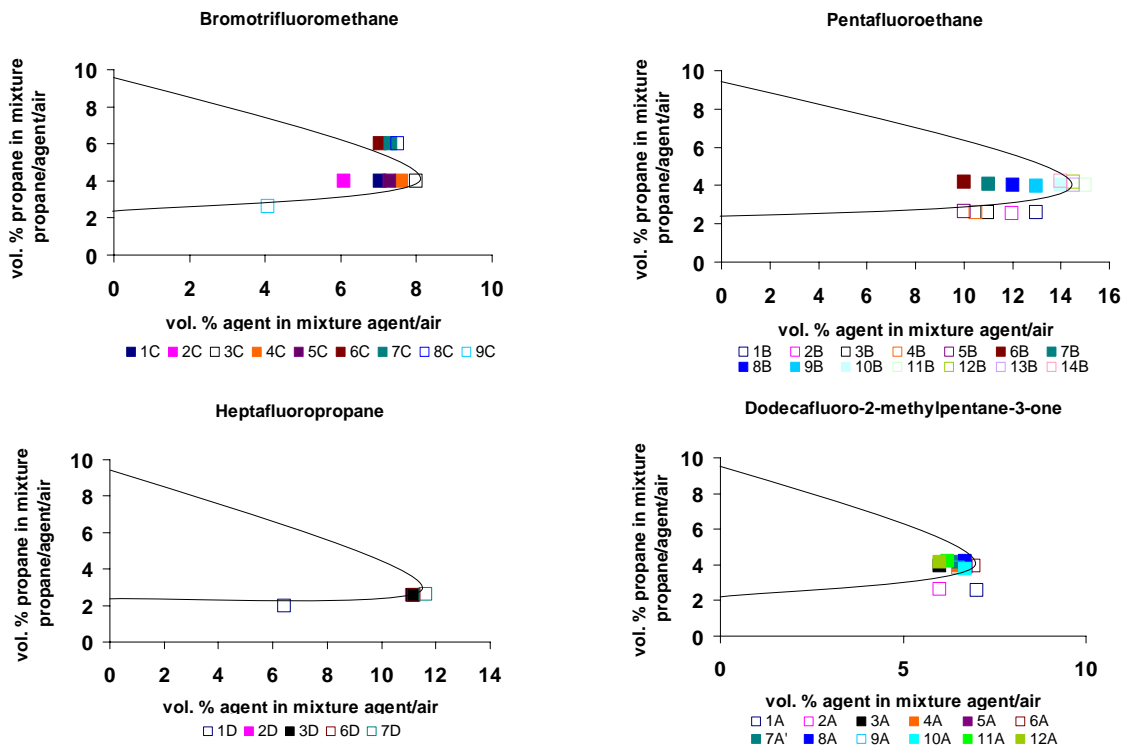


Figure 11. Diagrams presenting experiments in 8-litres bombs in order to determine inerting concentrations for different extinguishing agents. The fuel concentration is given as volume % propane in mixture of propane, extinguishing agent and air. The agent concentration is given as volume % extinguishing agent in mixture of extinguishing agent and air. Filled squares mark ignition and open squares mark no ignition

4.2 Flame extinguishing concentrations – Cup burner

The level of extinguishing concentrations for different extinguishing agents is commonly determined in the cup burner method. The results from cup burner tests with the four extinguishing agents tested are presented in Table 6. The results are also presented in Figure 12. Diagrams showing the change in concentration of extinguishing agent added to the propane flame in the cup burner test are shown in Figure 13 from tests with pentafluoroethane and dodecafluoro-2-methyl-pentane-3-one.

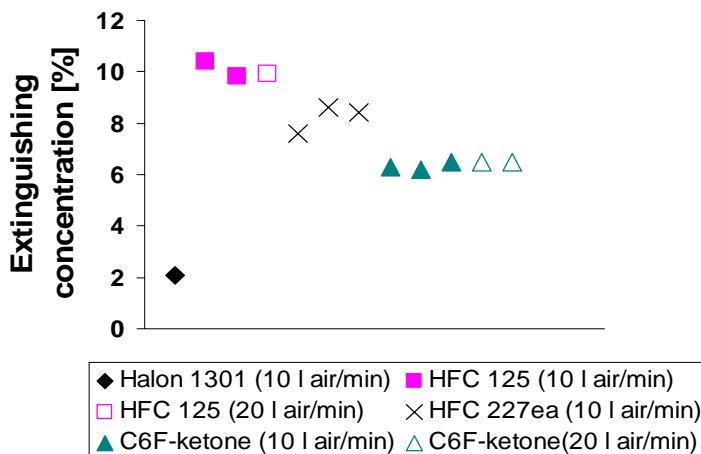


Figure 12. Extinguishing concentrations determined in the cup burner.

Table 6. Extinguishing concentrations determined in the cup burner.

Extinguishing agent	Flow propane	Flow air	Extinguishing concentration
	[l/min]	[l/min]	[vol. %]
CF₃Br			
	10	0.71	2.1
C₂HF₅			
	10	0.71	10.4
	10	0.71	9.8
	20	1.41	9.9
C₃HF₇			
	10	0.71	7.6
	10	0.71	8.6
	10	0.71	8.4
C₆F₁₂O			
	10	0.71	6.3
	20	1.41	6.5
	20	1.41	6.5
	10	0.71	6.2
	10	0.71	6.5

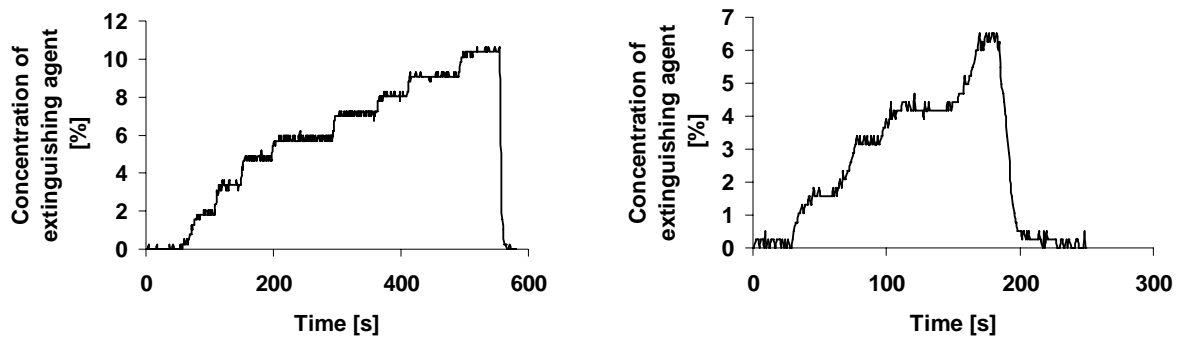


Figure 13. The diagrams show concentration of extinguishing agent added to a propane diffusion flame in the cup burner test. The test presented in the left diagram was performed with HFC 125 and in the right diagram results from a test with C₆F-ketone is presented.

4.3 Tubular burner

The main purpose with the experiments in the tubular burner set up was to study the breakdown products that are produced when an extinguishing agent is introduced into a flame. A list of the tests performed with the tubular burner is presented in Table 7.

Table 7. Test scheme for the burner tests with analysis of thermal break down products.

Extinguishing agent	Test	Extinction agent * (%)	Burner effect (kW)	Information on test
Halon 1301 (bromotrifluoromethane)	1301_1	51	1	Agent application for 3 min.
- " -	1301_2	86	1	Agent application for 5 min.
- " -	1301_3	56	1	Agent application for 5 min.
HFC 125 (pentafluoroethane)	125_1	10, 37, 67, 86	1	Gradually increase of agent. 5 min at each level. Extinguished at 86 %.
- " -	125_2	10	1	10 % agent concentration for 10 min.
- " -	125_3	37	1	37 % agent concentration for 10 min. Sampling of organic break-down products with activated carbon sampling tubes.
- " -	125_4	67	1	67 % agent concentration for 10 min.
- " -	125_5	86	1	The burner extinguished after 4 min
- " -	125_6	37	1	50 % agent concentration for 10 min. Sampling of HF with gas washing bottles.
HFC227ea (heptafluoropropane)	227_1	77, 82, 86, 91, 95	2	Gradual increase of agent until extinction
- " -	227_2	24, 65, 91, 100	1	Gradually increase of agent. 5 min at each level until extinction
- " -	227_3	24	1	24 % agent concentration for 5 min. Sampling of HF with gas washing bottles.
- " -	227_4	65	1	65 % agent concentration for 10 min. Sampling of organic break-down products with activated carbon sampling tubes.
- " -	227_5	91	1	91 % agent concentration for 5 min.
- " -	227_6	100	1	The burner extinguished after 3 min.
- " -	227_7	65	1	65 % agent concentration for 15 min (to investigate any possible drift on the FTIR measurement).
- " -	227_F1	24	1	Test of retention of HF in FTIR filter: 24% for 10 min.
- " -	227_F2	24	1	Test of retention of HF in FTIR filter: 24% for 20 min.
C₆F-ketone (dodecafluoro-2-methyl-pentane-3-one)	ketone_1	15	1	Agent application for 8 min. Note that C ₆ F-ketone is a liquid at room temperature.
- " -	ketone_2	37	1	Agent application for 10 min.
- " -	ketone_3	46	< 1	Agent application for 12 min. Sampling of organic break-down products with activated carbon sampling tubes.

* % of the REMP value

In order to find the amount of extinguishing agent that is needed to extinguish the flame the experiments were started by determining the Required Extinguishing Medium Portion, REMP. This is the specific amount of extinguishing agent required to extinguish the flame when fuel and extinguishing agent are fed concurrently into the burner. The REMP is given as the ratio between the mass flow of extinguishing agent to the mass flow of fuel, m_e / m_f . The REMP value is a quantitative measure of how efficient the agent is. A low REMP value indicates a more efficient agent than a high REMP value. The values from the tubular burner test performed in this project are presented in Table 8.

Table 8. REMP values for tested extinguishing agents.

Extinguishing agent	REMP value
Halon 1301	1.5
HFC 125	5.6
HFC 227ea	6.8
C ₆ F-ketone	15.4

4.3.1 Heat Production

It has been reported from earlier studies [20] that the Rate of Heat Released, RHR, from the flame is affected when an extinguishing agent is introduced into the flame. Since experiments were made with an agent that has been introduced quite recently the RHR was measured during the experiments in the tubular burner setup in order to study what influence this agent has on the RHR. The results are presented in Figure 14. The RHR was calculated according to the method given in the ISO cone calorimeter method, Eq 1. [21]

$$\dot{q} = (\Delta h_c / r_o) \cdot (1.10) \cdot C \cdot \sqrt{\frac{\Delta p}{T_e}} \cdot \frac{x_{O_2}^0 - x_{O_2}}{1.105 - 1.5 \cdot x_{O_2}} \quad \text{Eq. 1}$$

Where $\Delta h_c / r_o$ for propane was used with a value of $12.73 \cdot 10^3$ kJ/kg, 1.10 is the ratio of the molecular weights of oxygen and air, C is a calibration constant for the equipment, Δp is the pressure difference in Pa measured in the exhaust duct and T_e is the temperature in K measured at the same point as the pressure difference. $x_{O_2}^0 - x_{O_2}$ is the reduction in oxygen concentration between the initial value of oxygen analyzer reading and the actual oxygen analyzer reading, in mole fraction of oxygen.

It was found that HFC 125 and HFC 227ea give a rise in the heat release as expected and that Halon 1301 gives a reduction in the RHR when added to the flame. This behaviour has also been reported earlier by Holmstedt et al. [20]. The more recently introduced extinguishing agent C₆F-ketone did not give any significant contribution to the RHR.

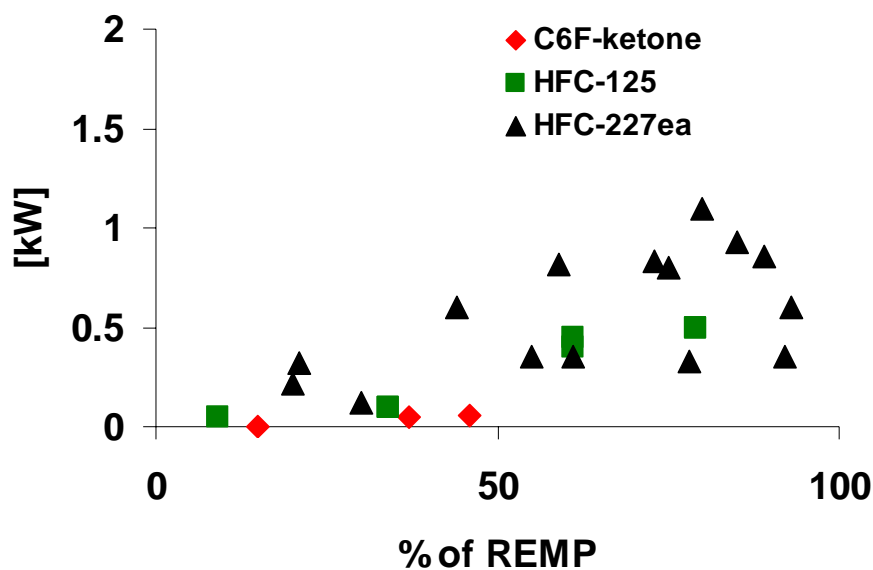


Figure 14. The energy contribution from the extinguishing agent added to the propane flame presented as a function of the proportion of agent to the REMP value.

4.4 Combustion products

Continuous measurements were made of CO, CO₂ and O₂. The results from the O₂ measurements were used in the calculation of RHR as presented. CO and CO₂ were measured both with conventional IR technique and with FTIR. Results from both measurements are presented in Figure 15 and Figure 16 for test 1 with HFC125. As can be seen there is a difference between the results from the two measurement methods for CO. It is known that when COF₂ is present in the analysed gas sample there is interference between CO and COF₂ in the FTIR measurements. A correction for this interference was made in the presented measurements but since the amount of COF₂ was high the correction might not have been sufficient, hence the difference between the presented results from IR and FTIR measurements. It can be seen in Figure 15 that when the amount of extinguishing agent is increased the difference between the IR and the FTIR measurements is also increased.

The production of CO in experiments with the four tested extinguishing agents is presented in Figure 15, Figure 17, Figure 19 and Figure 21. It was found that for all four agents the production of CO originates mainly from the extinguishing agent and not from the fuel.

The production of CO₂ for experiments with the four tested extinguishing agents is presented in Figure 16, Figure 18, Figure 20 and Figure 22. As can be seen in Figure 16 the discrepancy between the measuring methods is very small for CO₂. The production of CO₂ is highly dependant on the added amount of extinguishing agent, but as expected the fuel also contributes to the production of CO₂.

Production of CO and CO₂ from all experiments is presented in Annex A.

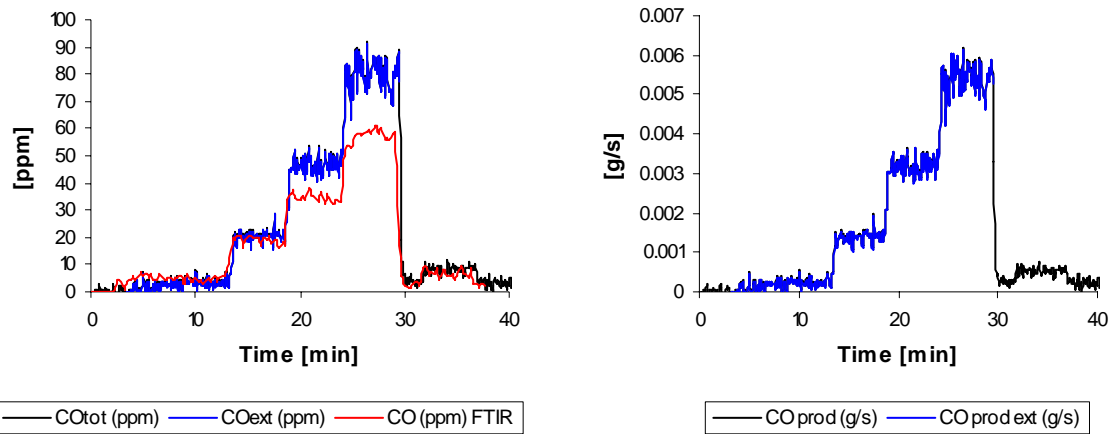


Figure 15. Production of CO as a function of time from test 1 with HFC 125. In the left diagram it is presented as volume fraction and in the right diagram as production in g/s

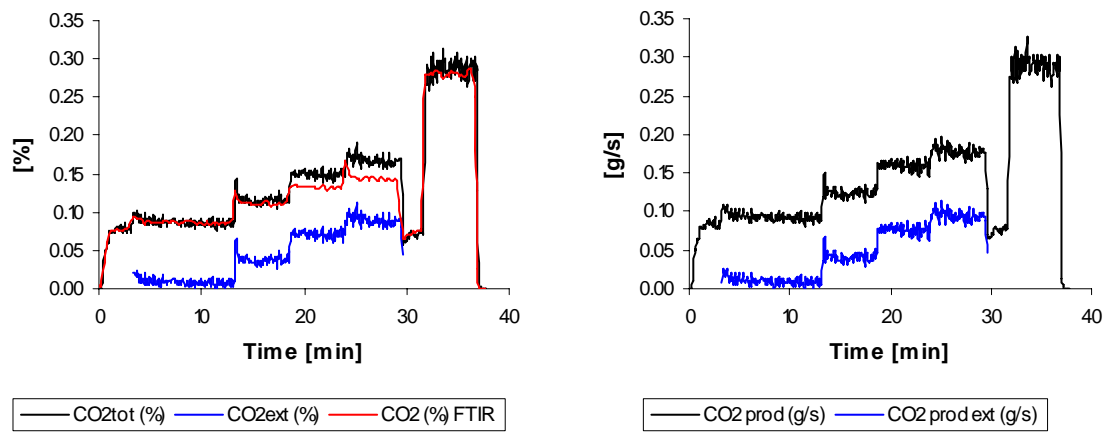


Figure 16. Production of CO₂ as a function of time from test 1 with HFC 125. In the left diagram it is presented as volume fraction and in the right diagram as production in g/s.

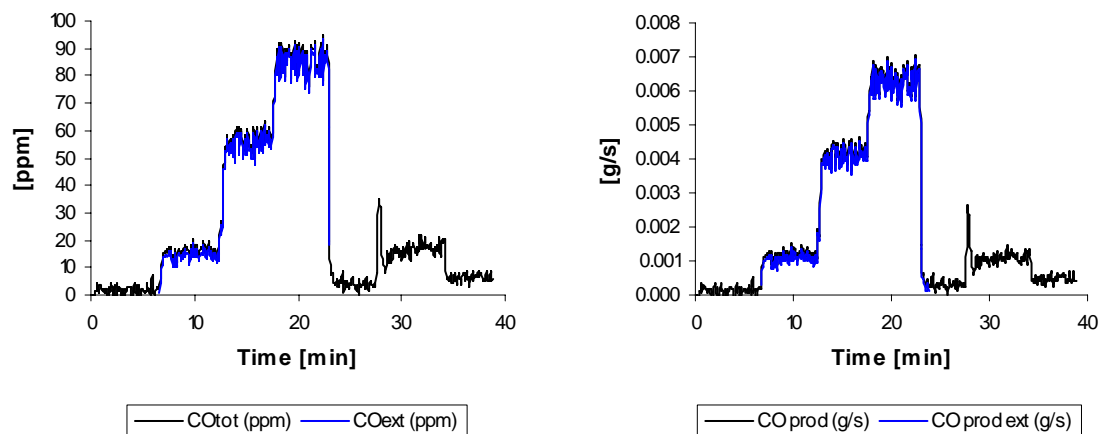


Figure 17. Production of CO as a function of time from test 2 with HFC 227ea. In the left diagram it is presented as volume fraction and in the right diagram as production in g/s.

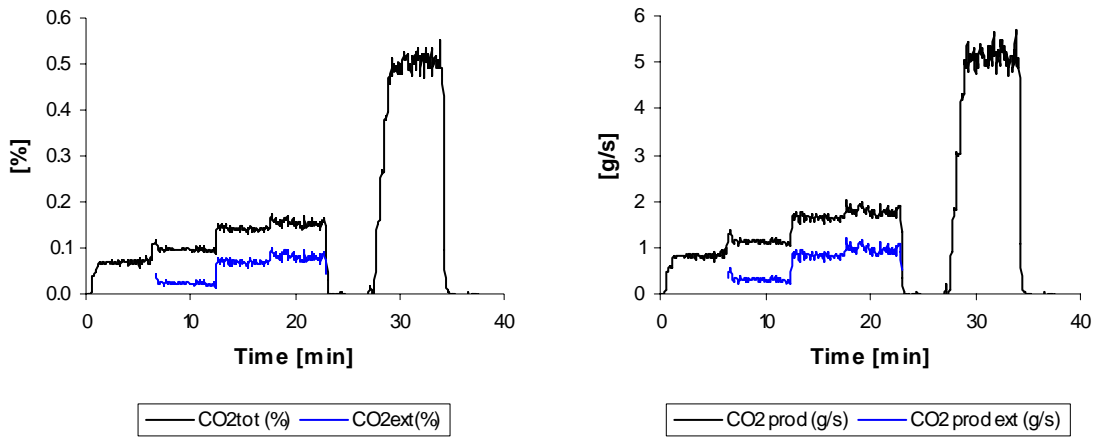


Figure 18. Production of CO₂ as a function of time from test 2 with HFC 227ea. In the left diagram it is presented as volume fraction and in the right diagram as production in g/s.

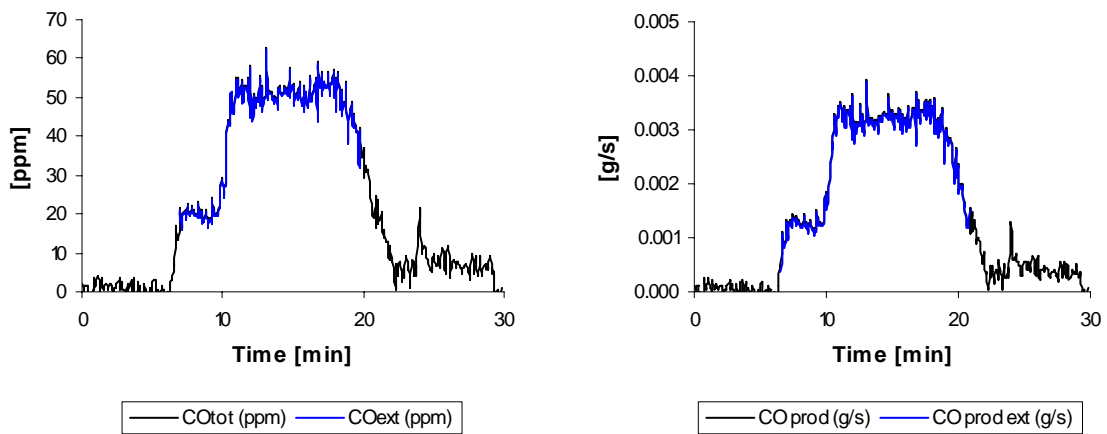


Figure 19. Production of CO as a function of time from test 3 with C₆F-ketone. In the left diagram it is presented as volume fraction and in the right diagram as production in g/s.

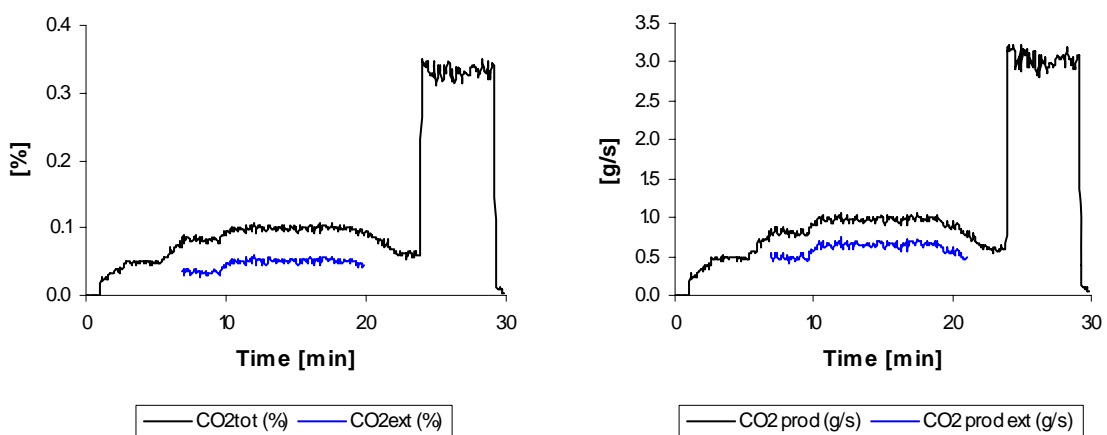


Figure 20. Production of CO₂ as a function of time from test 3 with C₆F-ketone. In the left diagram it is presented as volume fraction and in the right diagram as production in g/s.

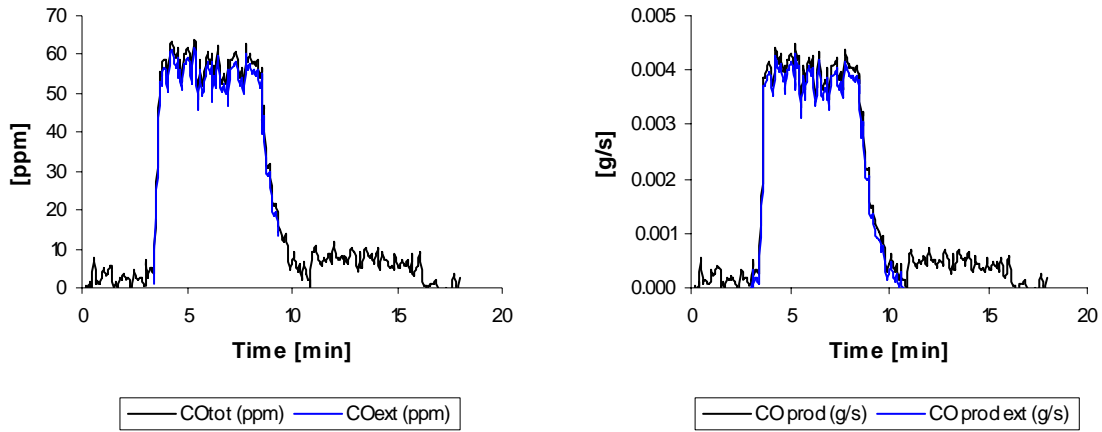


Figure 21. Production of CO as a function of time from test 3 with Halon 1301. In the left diagram it is presented as volume fraction and in the right diagram as production in g/s.

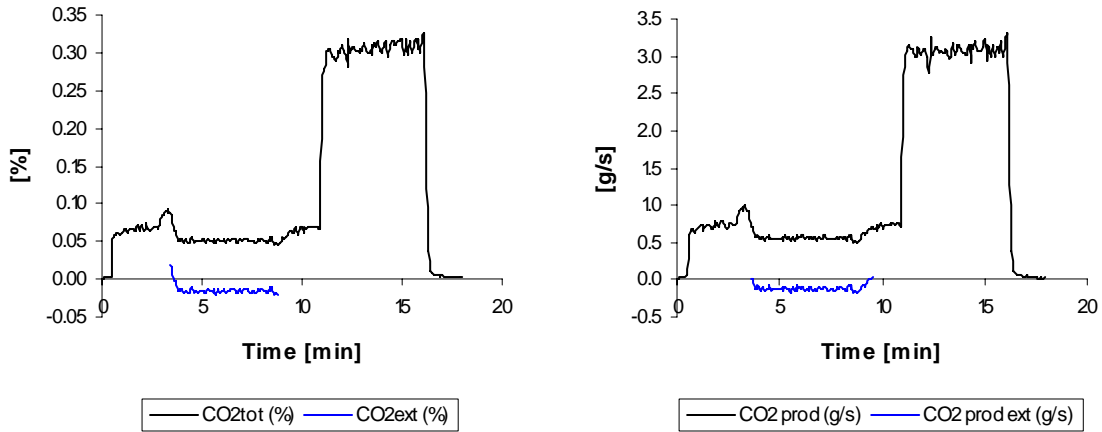


Figure 22. Production of CO₂ as a function of time from test 3 with Halon 1301. In the left diagram it is presented as volume fraction and in the right diagram as production in g/s.

4.5 Smoke production

The smoke production can be presented in a number of ways. In this report, the extinction coefficient K [1/m] is defined as in Eq. 2 from reference [22]:

$$K = \sigma_m \cdot m \quad \text{Eq. 2}$$

Where σ_m is the extinction area per unit mass [m^2/g] and m is the mass concentration of the smoke aerosol [g/m^3]. From the measurements in the duct, K is calculated as given by Eq. 3 below:

$$K = \left(\frac{I}{L}\right) \cdot \ln\left(\frac{I_0}{I}\right) \quad \text{Eq. 3}$$

Where L [m] is the beam length of the light through smoke. The channel in which the measurements were made was 0.114 m in diameter. I_0 [-] is the light intensity without smoke and I [-] is the light intensity during the test.

Representative examples of results from smoke measurements are presented in Figure 23 and Figure 24. The results from all experiments are given in Annex B. In Figure 25 results from all experiments are presented as a function of the amount of added extinguishing agent. The amount of added agent is expressed as % of the REMP-value. As can be seen the size of K is low for small quantities of HFC125 and HFC227ea and then increases to a maximum value for K at around 50% of REMP and then K decreases when more agent is added. For the other two agents the number of tested combinations is too low to enable any conclusions to be drawn about the relations between the amounts of added extinguishing agent and the value of K . The value of K for the period when only fuel is present is around 0.05 1/m in all experiments.

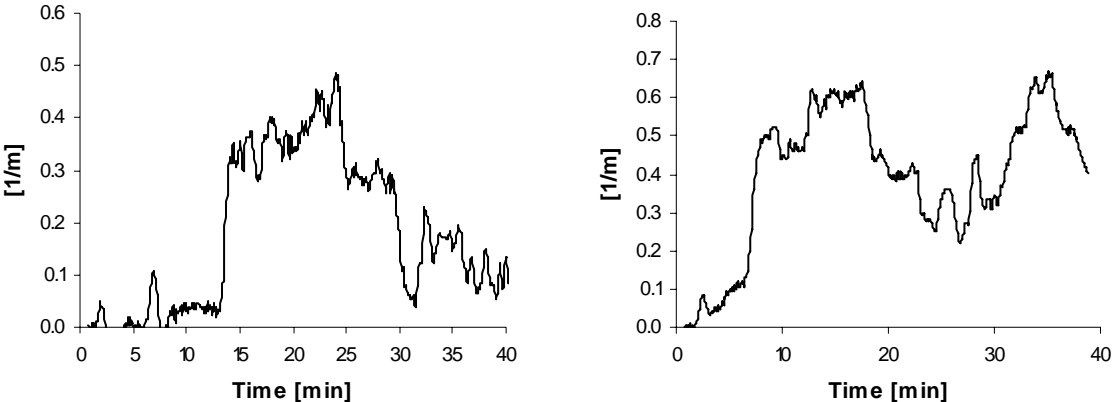


Figure 23. The extinction coefficient K from experiments with HFC125 is presented in the left hand figure and from experiments with HFC227ea in the right hand figure.

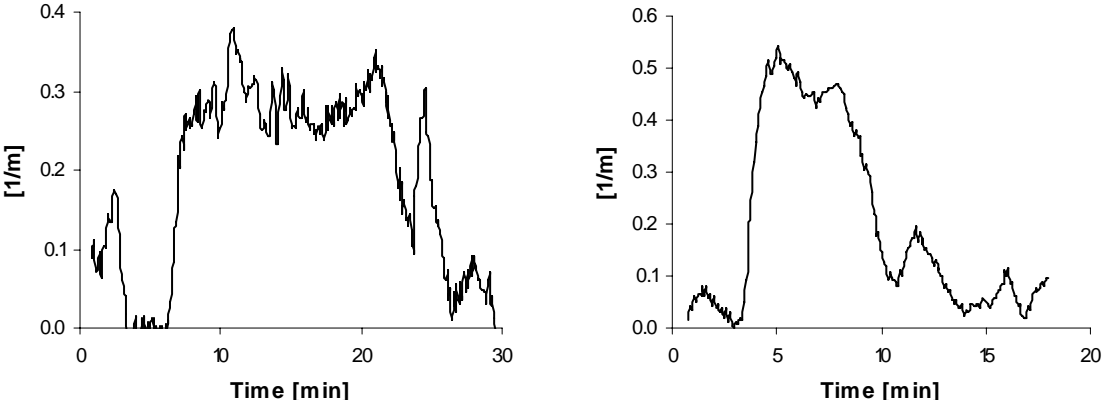


Figure 24. The extinction coefficient K from experiments with $C_6F_{12}O$ is presented in the left hand figure and from experiments with Halon 1301 in the right hand figure.

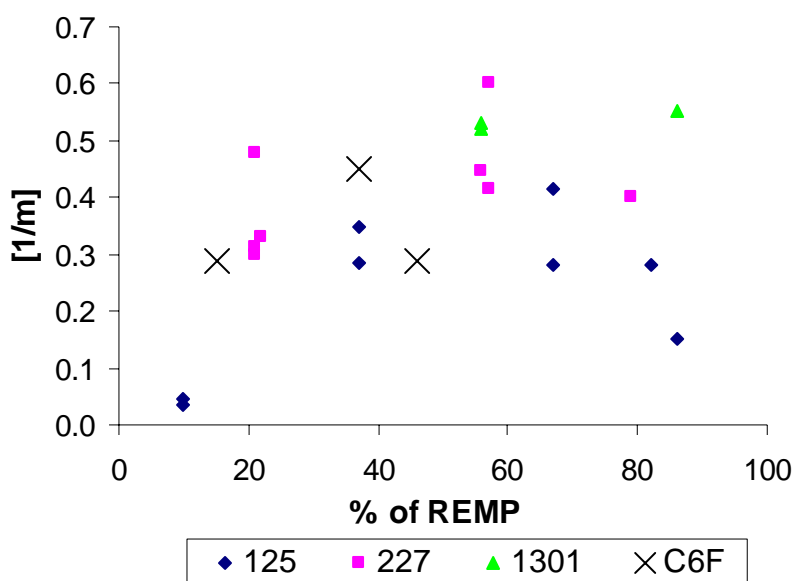


Figure 25. The extinction coefficient K for experiments with all extinguishing agents is presented as function of the amount of applied extinguishing agent relative to the REMP value.

4.6 Production of halogenated compounds

Measurement of halogen containing combustion products was made principally with FTIR technique. The FTIR measurements revealed the production of HF and also COF_2 in the tests with all four extinguishing agents. In the case of Halon 1301, the production of HBr was further determined. Also halogenated organic compounds absorb IR radiation and are shown in the FTIR spectrum. A qualitative evaluation of these compounds has been made from the FTIR spectra. Additionally, gas samples were sampled on activated carbon sampling tubes in one test with each extinguishing agent. These samples were analysed for halogenated organics using GC-MS technique.

Selected results from these analyses are given together with a discussion in the main body of the report. A full account of the detailed results is given in Annex C.

The yields of HF and COF_2 found in the tests are shown in Figure 26. For example, in Figure 26 (a) the results from all tests conducted with HFC 227ea are plotted versus the relative application rate of the extinguishing agent. The yields are expressed as the quotient of the production rate of the halogenated compound and the application rate of HFC 227ea. The relative application rate of HFC 227ea on the x-axis is expressed as the application rate relative the REMP value. The REMP value corresponds to the application rate for extinction (100%).

It is clear from Figure 26, that both HF and COF_2 are produced from all four extinguishing agents. The yield of HF decreases for HFC 227ea, HFC 125 and $\text{C}_6\text{F}_{12}\text{O}$ with an increased application rate of the extinguishing agent. The yield of HF is very high for both HFC 227ea and HFC 125, about 0.7 g/g at low relative application rates. The yield of HF from $\text{C}_6\text{F}_{12}\text{O}$ is significantly lower at low relative application rates. No results are available for high relative application rates. The yield of HF from Halon 1301 is rather constant at the two relative application rates investigated, about 0.4 g/g. The yield of COF_2 instead increases with an increased application rate for all extinguishing agents. Probably, at low relative application rates the organic extinguishing agent is largely combusted and fluorine is effectively transferred to HF.

At higher relative application rates, where the extinction effect becomes more evident, the combustion of the extinguishing agent is less effective and the formation of COF_2 is preferred before HF.

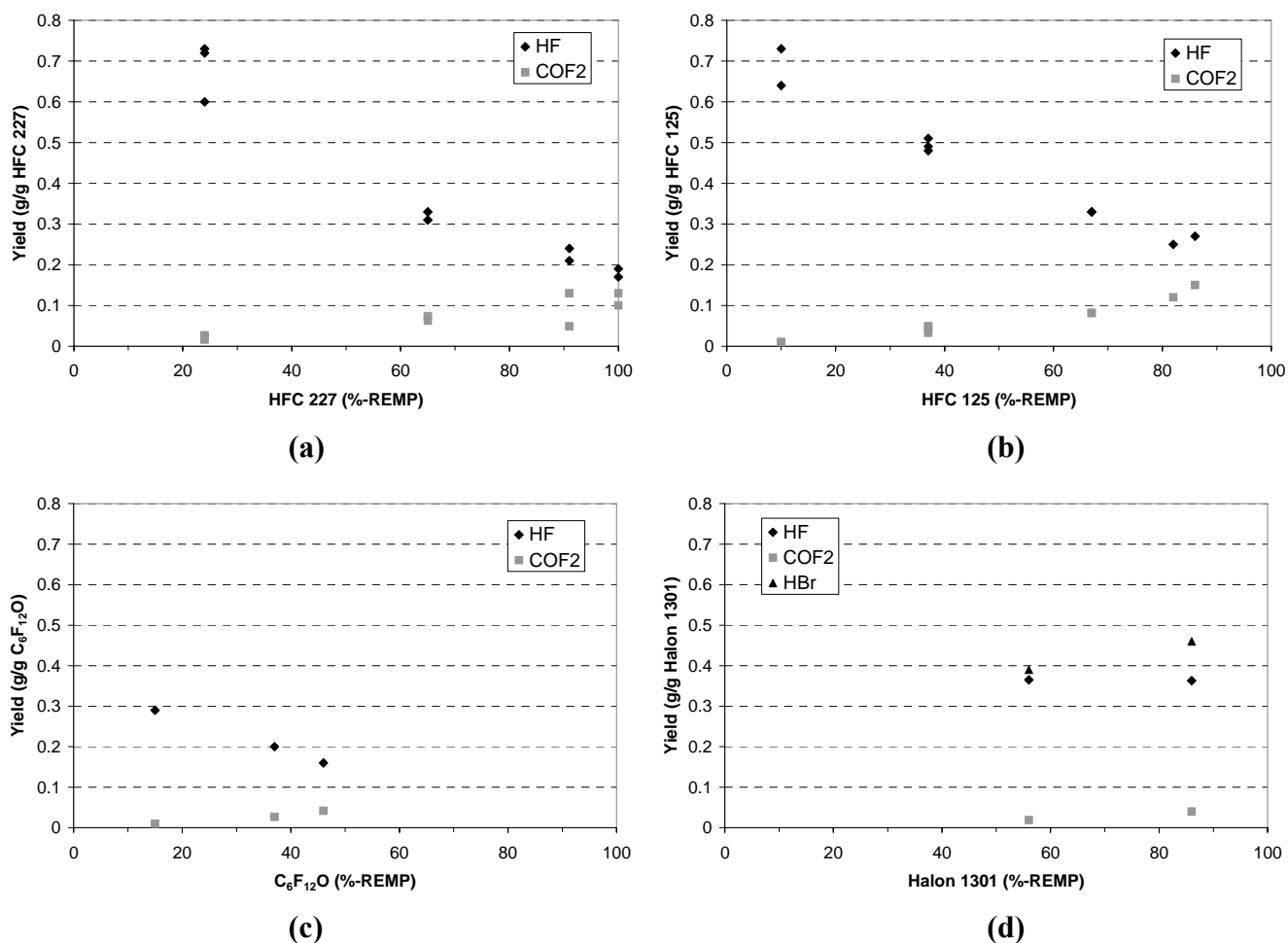


Figure 26. Yields of halogen containing combustion products from the tests with: (a) HFC 227ea, (b) HFC 125, (c) C₆F₁₂O and (d) Halon 1301.

The data in Figure 26 is presented as yields, *i.e.* mass of combustion product produced per mass of extinguishing agent applied. The data in Figure 26 give thus no direct information on the amounts of combustion products produced in fires if comparing the four tested extinguishing agents. In order to make a comparison possible the yields for each extinguishing agent have been multiplied with respective REMP-value. This normalized yield data is presented in Figure 27.

Figure 27 shows that, at lower relative application rates, the absolute production of HF from C₆F₁₂O is comparable with that from HFC 227 and HFC 125. That is, even if the yield of HF from C₆F₁₂O is lower, the absolute production is large due to the high REMP-value. Figure 27 further shows that the absolute production of HF from Halon 1301 is significantly lower compared to the new alternative extinguishing agents.

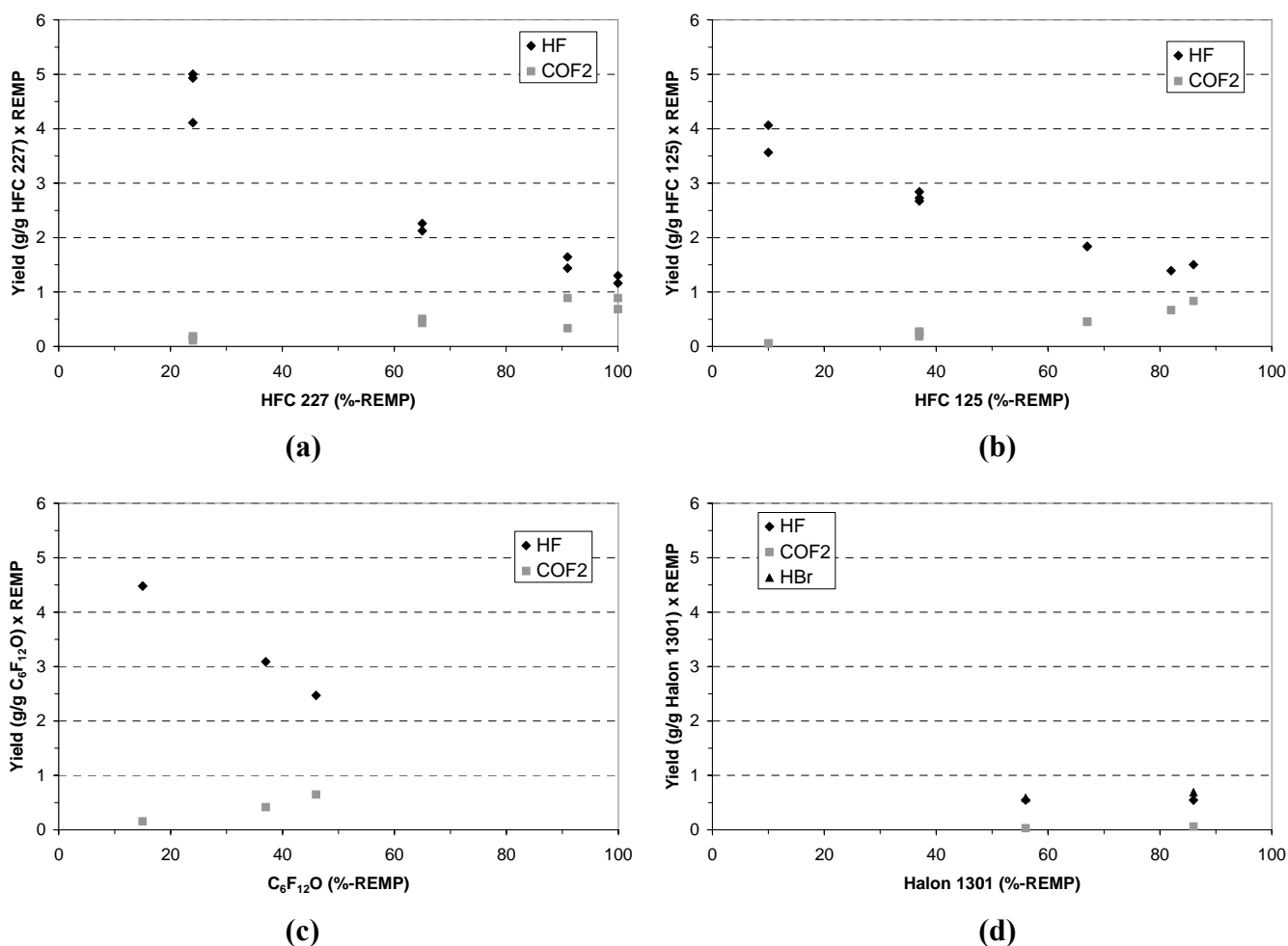


Figure 27. Yields of halogen containing combustion products, normalized against the REMP value, from the tests with: (a) HFC 227- REMP = 6.8, (b) HFC 125 - REMP = 5.6, (c) C₆F₁₂O - REMP = 15.4 and (d) Halon 1301 - REMP = 1.5.

The recovery of fluorine as HF and COF₂ has been calculated for the extinguishing agents and is presented in Figure 28. The main fraction of fluorine ends up as HF for HFC 227 and HFC 125 at lower relative application rates. Closer to extinguishing concentrations the fraction recovered as COF₂ increases, but the total recovery of fluorine including HF is below 40 % at 90 % relative application rate. The recoveries of fluorine as HF and COF₂ for C₆F₁₂O is lower compared to HFC 227 and HFC 125. There is a clear difference in the recovery for Halon 1301 where an almost quantitative recovery as HF or COF₂ is found for fluorine. Halon 1301 contains bromine also, which to a large part is recovered as HBr.

There is always a risk for losses in sampling of compounds like HF and HBr as these compounds tend to get dissolved in any condensed water in the sampling train. That was the reason for using heated sampling lines and filter. Although a heated sampling train is used there are always some losses in sampling. The amount of HF and HBr retained by the heated ceramic filter positioned before the FTIR was analysed in some of the tests. The filters were leached in hot water and subsequently analysed for F⁻ and Br⁻ with ion chromatography (IC). The results of this investigation are presented in Table C9 and Table C10. The general trend regarding losses of HF was that the losses were in the range of 1 – 5 relative-percent, and it seems likely that the losses decreases for a filter after prolonged use. The losses in a filter for a 10 min sampling period was 2.2 relative-percent, whereas the losses for a 20 min period sampling of the same quality of fire

gas atmosphere was 1.0 relative-percent only. The losses of HF were thus rather small and the values of recoveries presented in Figure 28 are only underestimated with a few relative percents.

During the tests gas samples were also taken to be analysed with ion chromatography. However the losses during the process of taking the samples was large so the results were about a factor of ten lower than the FTIR measurements.

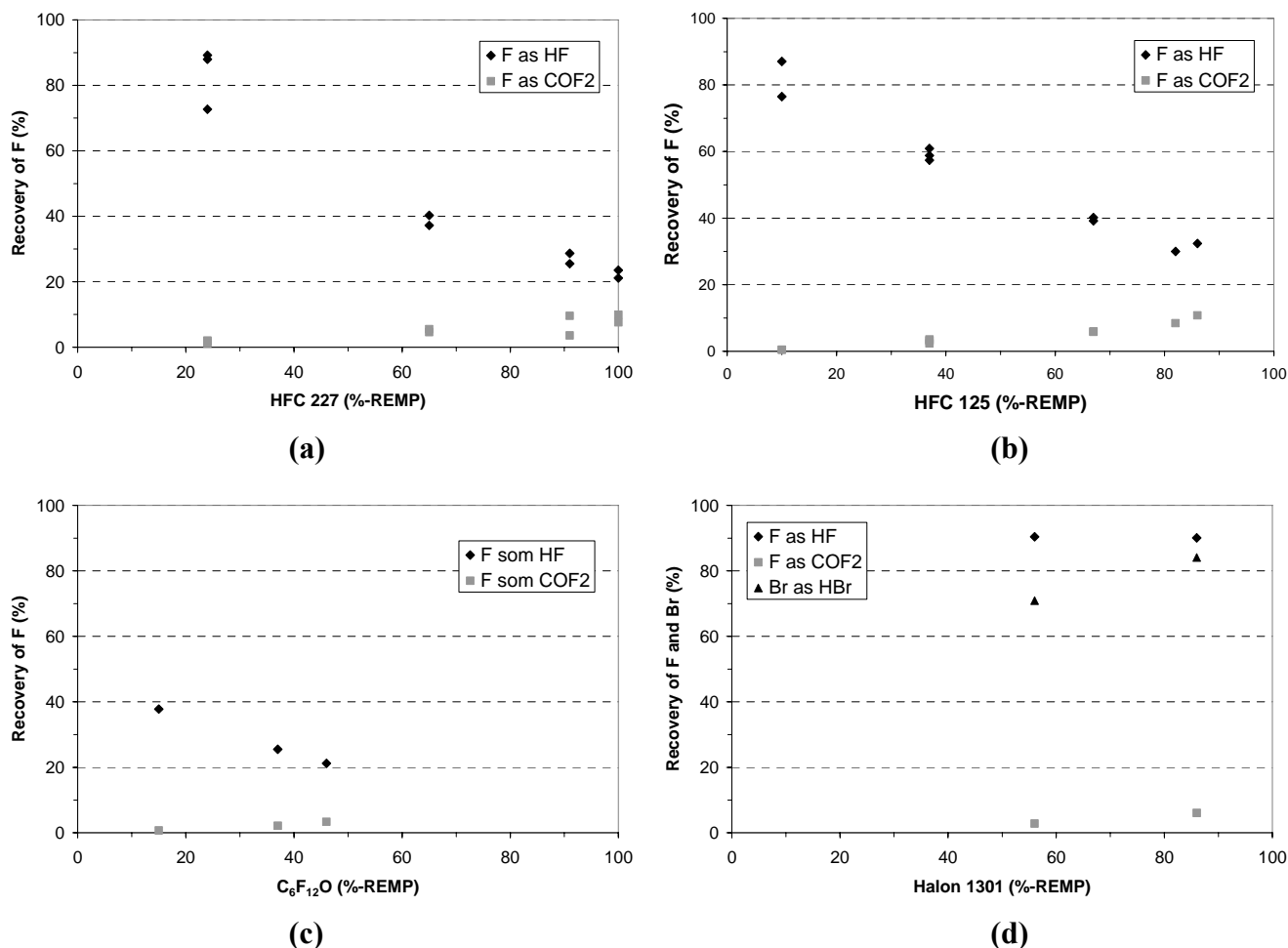


Figure 28. Recoveries of fluorine (and bromine in one case) from the tests with: (a) HFC 227, (b) HFC 125, (c) $C_6F_{12}O$ and (d) Halon 1301.

4.5.1 Qualitative analysis of FTIR measurements

It is clear from Figure 28 that fluorine containing organic break-down products or survival fractions of the extinguishing agent must be present in the fire gases, especially in the tests with high relative application rates. Notably in the cases of the three halon replacement agents, the recovery of fluorine as HF and COF_2 is low and the recovery as organics must be high.

The molecule of a fluorine-containing extinguishing agent and the organic break-down products of the agent absorb IR radiation and are visible in FTIR spectra. FTIR spectra from the tests are shown below.

For each extinguishing agent there are three spectra shown. The first spectrum is from a measurement of a mixture of the extinguishing agent in air. A known flow rate of the agent was

released through the (non-burning) burner and was collected and measured in the smoke gas hood of the cone calorimeter in the normal way. The second spectrum is from a test with a low relative application rate of the agent. The third spectrum is from a test with a rather high relative application rate.

FTIR spectra of HFC 227ea are shown in Figure 29. The HFC 227ea molecule consists of a propane backbone substituted with seven fluorine atoms and one hydrogen atom. The (top) spectrum in Figure 29 is showing the spectral fingerprint of HFC 227ea with a number of absorbance peaks from the many possible vibrational modes of the molecule.

In the spectrum from a combustion test with an application rate of 24 %-REMP (middle) none of the peaks from the pure agent can be seen, instead are peaks from HF and CO₂ dominating. There is, however, one peak at 1027.2 cm⁻¹ which is from a break-down product of HFC 227ea. The bottom spectrum in Figure 29 is from a test with an application rate of 91 %-REMP. The flame is thus close to extinction and a new product pattern can be seen from the IR spectrum. In addition to HF and CO₂, absorption peaks from COF₂ have also appeared. The IR spectrum of pure COF₂ mixed with nitrogen is shown overlaid on the 91 %-REMP spectra in Figure 30.

There are further a number of peaks in the 91 %-REMP spectra indicating survival fractions of the extinguishing agent. The peak at 1027 cm⁻¹ does also appear in this spectrum, and has grown considerably compared to the spectrum from the 24 %-REMP test. The 1027 cm⁻¹ peak is probably from an organic break-down product. The molecular vibration responsible for the peak has not been identified but it seems reasonable that it should be some type of C-F vibration. As an example, the C-F stretch in CH₃F gives a peak at 1049 cm⁻¹.

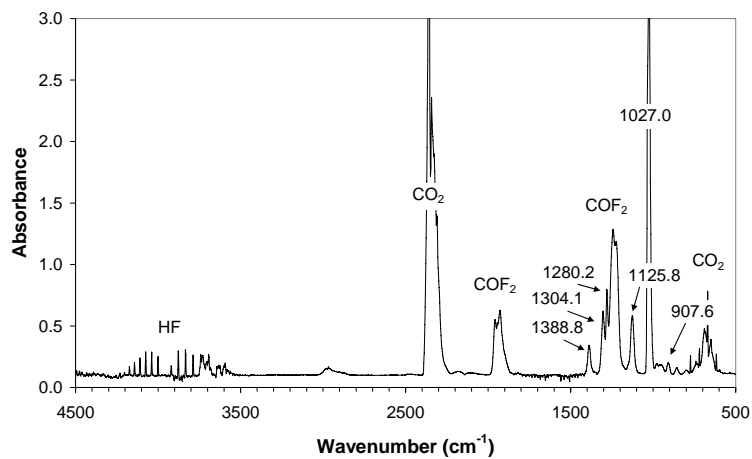
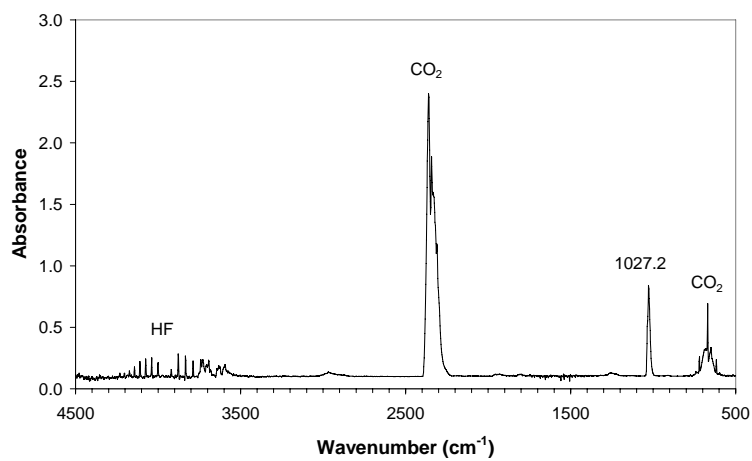
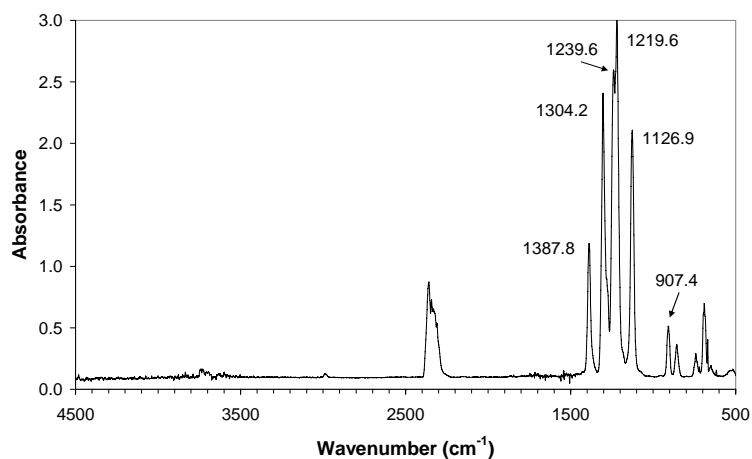


Figure 29. FTIR spectra from: (top) approx. 640 ppm HFC 227ea mixed in air, (middle) combustion test with 24 %-REMP HFC 227ea, (bottom) combustion test with 91 %-REMP HFC 227ea.

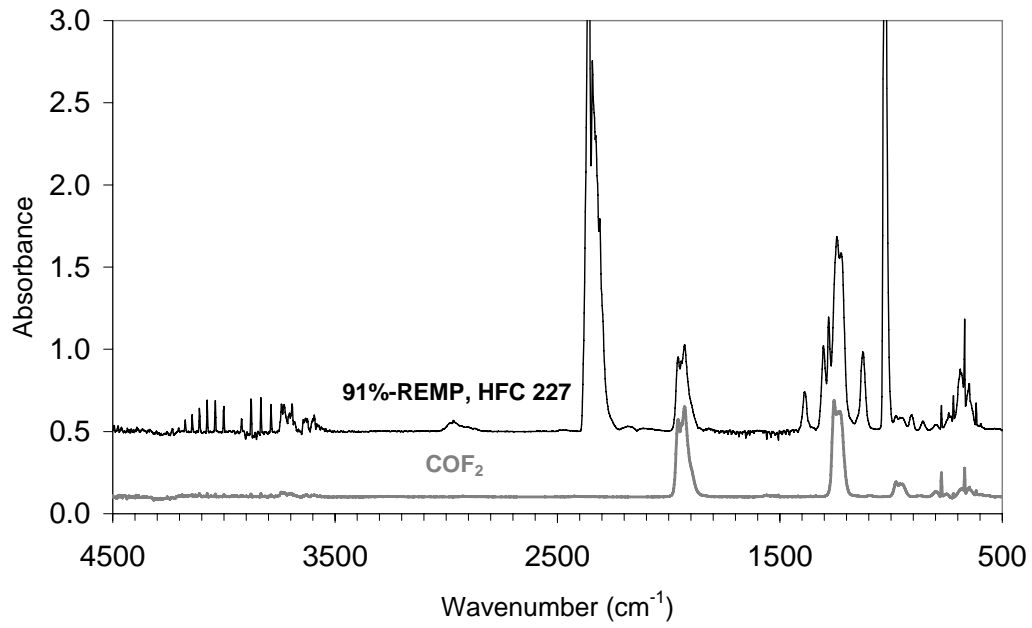


Figure 30. FTIR spectrum of combustion test with 91 %-REMP HFC 227ea overlaid with spectrum of COF₂.

FTIR spectra of HFC 125 are shown in Figure 31. The HFC 125 molecule consists of an ethane back bone substituted with five fluorine atoms and one hydrogen atom. The (top) spectrum in Figure 31 is showing the spectral finger print of HFC 125 with three major absorbance peaks. The middle spectrum is showing the spectrum from a test with 10 %-REMP. The spectral features of HF are visible here, and also a small peak at 1027.2 cm^{-1} indicating some organic break-down product. In the bottom spectrum in Figure 31, the spectral features of COF_2 are clearly visible, and the peak at 1027.2 cm^{-1} has grown considerably indicating a high portion of organic break-down products. No survival fraction of the extinguishing agent can be seen in the spectrum.

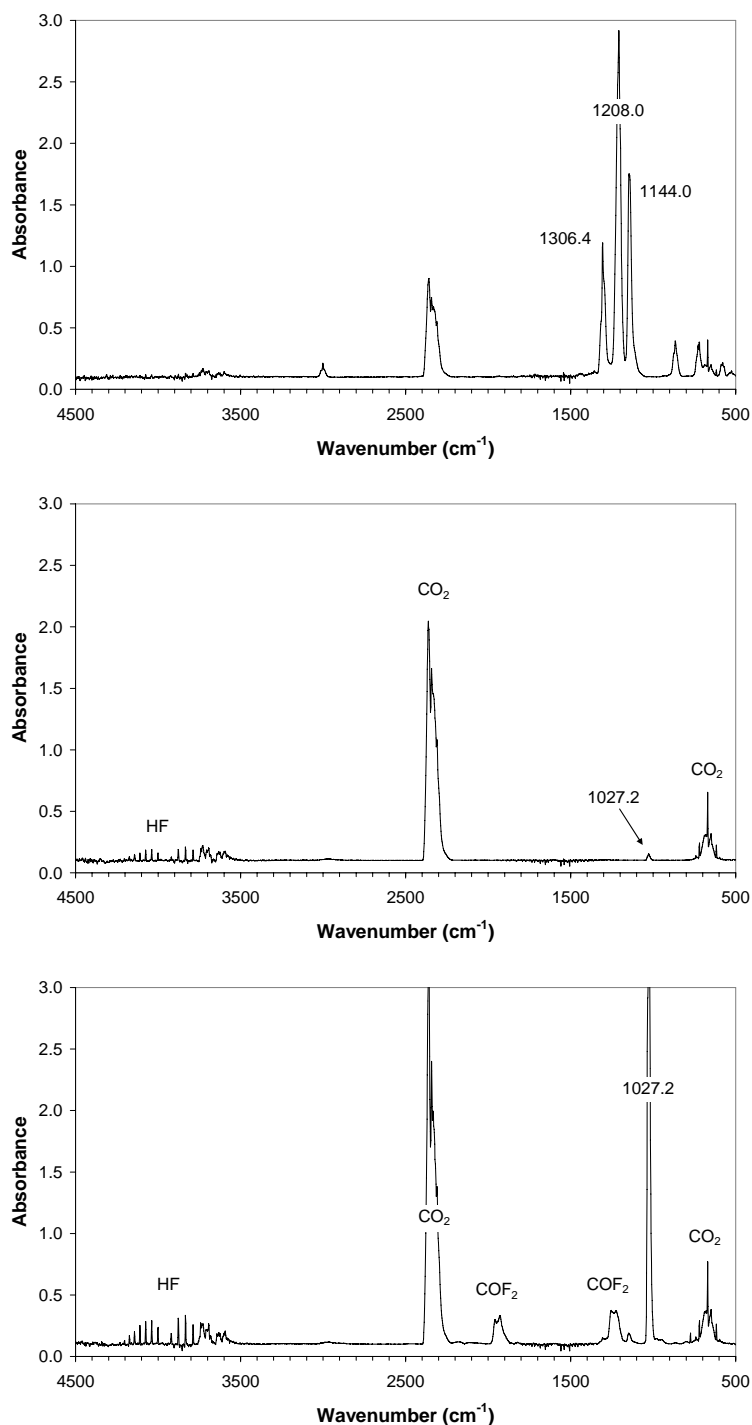


Figure 31. FTIR spectra from: (top) approx. 250 ppm HFC 125 mixed in air, (middle) combustion test with 10 %-REMP HFC 125, (bottom) combustion test with 67 %-REMP HFC 125.

FTIR spectra of $C_6F_{12}O$ are shown in Figure 32. The $C_6F_{12}O$ molecule is rather large and complex and separates itself somewhat from the other two halogen replacement agents by containing an oxygen atom. The (top) spectrum in Figure 32 is showing the spectral finger-print of $C_6F_{12}O$ with two major absorbance peaks around 1300 cm^{-1} and a C=O stretch peak at 1781.4 cm^{-1} . The middle spectra is from a combustion test with 15 %-REMP and the bottom spectra is from a test with 46 %-REMP. These spectra reminds very much of the corresponding spectra for HFC 125 shown in Figure 31. The peak at 1027.2 cm^{-1} is as in the case of HFC 125 and HFC 227ea also typical for the break-down products of $C_6F_{12}O$.

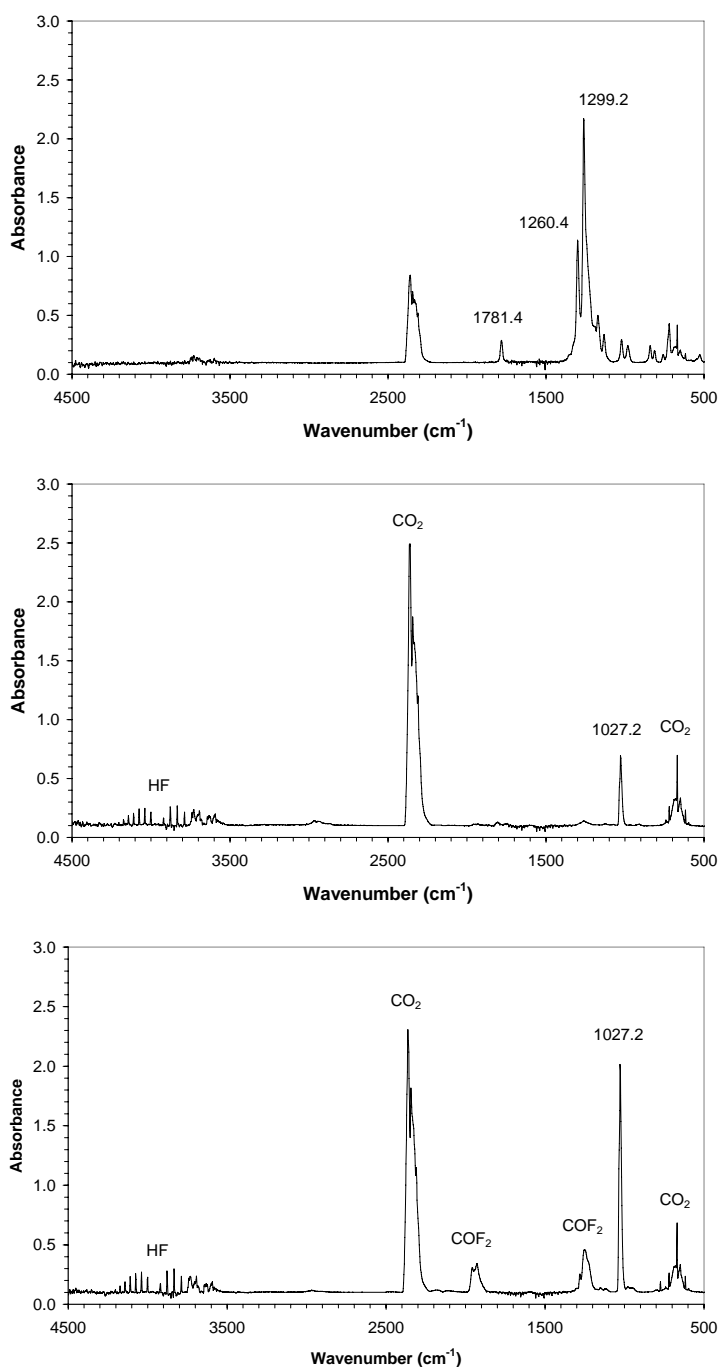


Figure 32. FTIR spectra from: (top) approx. 170 ppm $C_6F_{12}O$ mixed in air, (middle) combustion test with 15 %-REMP $C_6F_{12}O$, (bottom) combustion test with 46 %-REMP $C_6F_{12}O$.

FTIR spectra of Halon 1301 are shown in Figure 33. The Halon 1301 molecule is rather simple, consisting of a carbon atom substituted with three fluorine atoms and one bromine atom. The (top) spectrum in Figure 33 is showing the spectral finger print of Halon 1301 with two major absorbance peaks from CF₃-stretches. C-Br vibrations are not seen in the spectrum as these are present below 500 cm⁻¹ [23].

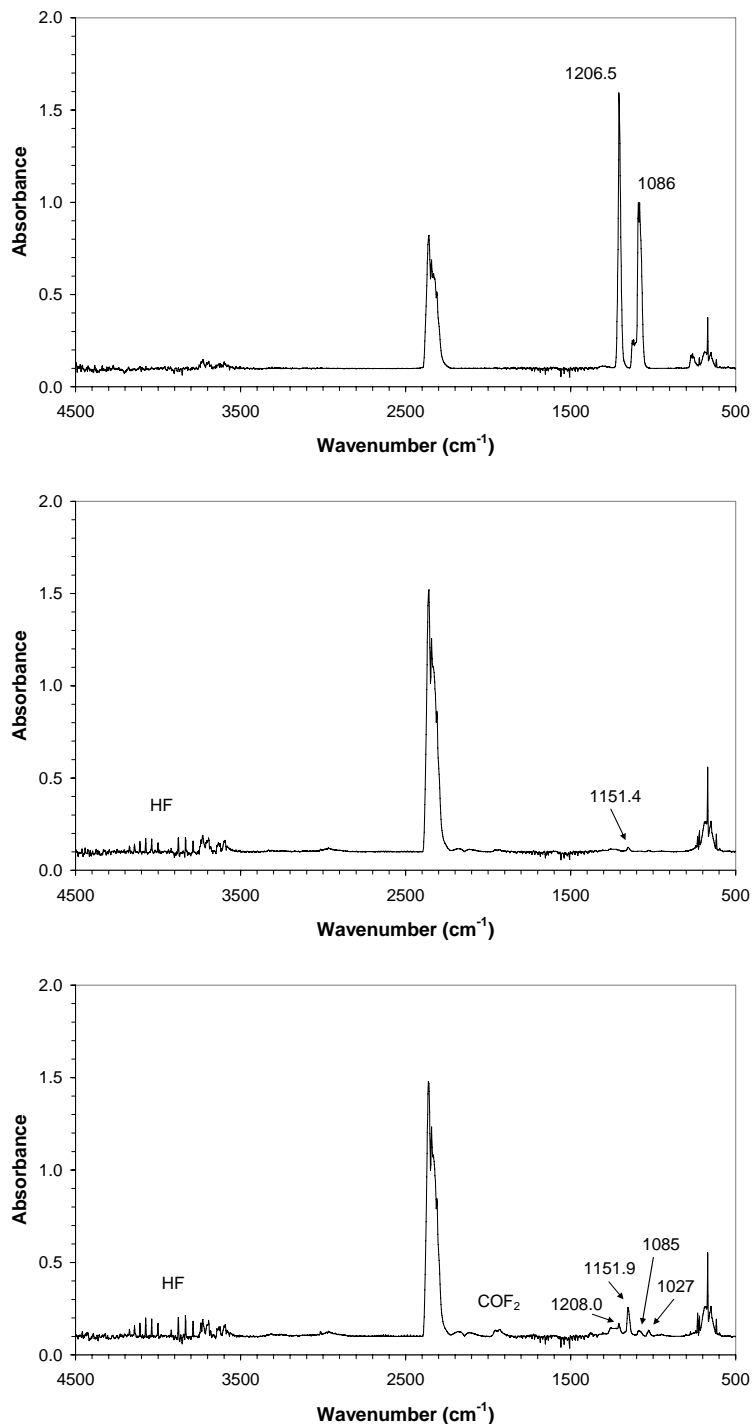


Figure 33. FTIR spectra from: (top) approx. 80 ppm Halon 1301 mixed in air, (middle) combustion test with 56 %-REMP Halon 1301, (bottom) combustion test with 86 %-REMP Halon 1301.

The middle spectra in Figure 33 is from a combustion test with 56%-REMP and the bottom spectra is from a test with 86%-REMP. The spectral features of HF are present in both spectra.

In the 86 %-REMP test also the spectra of COF_2 is visible together with the two peaks from CF_3 -stretches indicating survival fractions of the extinguishing agent. There is also a peak around 1152 cm^{-1} which indicates some organic break-down product. A weak peak at 1027 cm^{-1} is further present in the 86 %-REMP spectrum.

4.5.2 Results from GC-MS measurement

Samples were taken on activated carbon sampling tubes for subsequent GC-MS analysis of organic break-down products. This type of samples was taken in test 227_4 with HFC 227ea, in test 125_3 with HFC 125 and in test $\text{C}_6\text{F}_{12}\text{O}_3$ with $\text{C}_6\text{F}_{12}\text{O}$.

The results of the GC-MS analysis were quite dissatisfactory in that it was difficult to identify organic break-down products with any reasonable accuracy. The reason was a non-optimized analysis system. However, some results were attained.

For HFC 227ea the GC separation revealed an early peak with a retention time (~ 3.27 min) between that of CO_2 and propane. Mass number 69, 151 and 82 were dominant at that retention time as showed by the MS analysis. This matches quite well to a database mass-spectrum of heptafluoropropane (HFC 227). A double-peak with a much longer retention time (16.28 min, 16.34 min) was further found, but the compounds in these peaks could not be identified. The major mass number at ~ 16.28 min, however, was 44, and the major mass number at ~ 16.34 min was 85.

Also for HFC 125 a small peak was found between that of CO_2 and propane (~ 3.27 min). At this retention time mass number 51, 101 and 69 were dominating. This could possibly indicate the presence of pentafluoroethane (HFC 125). The GC separation further showed a strong peak with a retention time slightly longer than that of CO_2 and propane. The dominating mass fragment in this peak had a mass number of 85. No conclusive identification was made, but one candidate substance with a significant mass number of 85 would be CF_3OH . The same type of double-peak as for HFC 227ea, with a long retention time, was also found for HFC 125.

For $\text{C}_6\text{F}_{12}\text{O}$ the GC separation showed a number of peaks with a retention time slightly longer than that of CO_2 and propane. Compounds identified from these peaks were 2-methylbutane, methylbutane, cyclo-pentene and cyclo-pentane (alternatively 1-pentene). A significant peak at a retention time of ~ 16.29 min was found for $\text{C}_6\text{F}_{12}\text{O}$. Fragments with mass number 69, 119, 44, 147, 169 and 197 were dominating at this retention time. The mass number of $\text{C}_6\text{F}_{12}\text{O}$ is 316 and it seems reasonable that the molecule is fragmented in 119 and 197 as the heaviest fragments. The parent molecule $\text{C}_6\text{F}_{12}\text{O}$ was thus identified from the GC-MS analysis.

5 CONCLUSIONS

Fire extinguishing agents are combustible and they thermally decompose at elevated temperatures. The flammability limits are higher when compared to ordinary fuels. However, the decomposition of fire extinguishing agents leads to the formation of toxic compounds such as HF and COF_2 . A number of chemical mechanisms of fire suppression agents have been provided in this study. One main path has been identified for formation of HF when Halon 1301 is applied to a fire. When Halon replacement agents are studied it is found that HF can be formed along the whole reaction chain, at initiation reaction, chain propagation reactions and termination reactions. The studies also show that COF_2 can be formed in reaction with most Halon replacement agents.

Inerting concentrations were determined for the four studied extinguishing agents with propane as fuel. The results are in good agreement with inerting concentrations presented in literature, taken into account that a number of fuels and equipments have been used in experiments reported by other authors. The tests show that inerting concentrations are lowest for CF_3Br and $\text{C}_6\text{F}_{12}\text{O}$, about 7 % and highest for C_2HF_5 , 14 % with C_3HF_7 in between with an inerting concentration of 11.5 %.

The extinguishing concentrations for the different agents were determined in the cup burner. The tests show that the extinguishing concentration is lowest for CF_3Br , with 2.1 % and highest for C_2HF_5 with an extinguishing concentration of 10 %. $\text{C}_6\text{F}_{12}\text{O}$ gives 6.5 % and C_3HF_7 8 % extinguishing concentrations.

The main part of the project was aimed at studying the breakdown products that are produced when an extinguishing agent is introduced into a flame. For this purpose a set up with a tubular burner was used.

Earlier studies have indicated that when extinguishing agents are introduced into a flame the RHR from the flame is influenced. It was found that HFC 125 and HFC 227ea give a rise in the heat release as expected and that Halon 1301 gives a reduction in the RHR when added to the flame. This behaviour has also been reported earlier by Holmstedt et al. [20]. The more recently introduced extinguishing agent C_6F -ketone did not give any significant contribution to the RHR.

During the experiments CO and CO_2 were measured continuously with both conventional IR techniques and with FTIR. When the results from the different measuring techniques are compared it is found that there is a difference between the results from the two measurement methods for CO. It is known that when COF_2 is present in the analysed gas sample there is interference between CO and COF_2 in the FTIR measurements. A correction for this interference was made in the presented measurements but since the amount of COF_2 was high the correction might not have been sufficient, hence the difference between the presented results from IR and FTIR measurements. It was found that when the amount of extinguishing agent is increased the difference between the IR and the FTIR measurement is also increased.

All extinguishing agents tested within the project contain halogen atoms. Consequently analysis of halogen containing combustion products was of interest. These analyses were made principally with FTIR technique. Production of HF and COF_2 was found in experiments with all four extinguishing agents. In experiments with Halon 1301 the production of HBr was also determined. It was found that the main fraction of fluorine ends up as HF for HFC 227 and HFC 125 at lower relative application rates. Closer to extinguishing concentrations the fraction recovered as COF_2 increases, but the total recovery of fluorine including HF is below 40 % at

90 % relative application rate. The recoveries of fluorine as HF and COF₂ for C₆F₁₂O is lower compared to HFC 227 and HFC 125. There is a clear difference in the recovery for Halon 1301 where an almost quantitative recovery as HF or COF₂ is found for fluorine. Halon 1301 contains bromine also, which to a large part is recovered as HBr.

The yield of HF decreases for HFC 227ea, HFC 125 and C₆F₁₂O with an increased application rate of the extinguishing agent. The yield of HF is very high for both HFC 227ea and HFC 125, about 0.7 g/g at low relative application rates. The yield of HF from C₆F₁₂O is significantly lower at low relative application rates. No results are available for high relative application rates. The yield of HF from Halon 1301 is rather constant at the two relative application rates investigated, about 0.4 g/g. The yield of COF₂ instead increases with an increased application rate for all extinguishing agents. Probably, at low relative application rates the organic extinguishing agent is largely combusted and fluorine is effectively transferred to HF. At higher relative application rates, where the extinction effect becomes more evident, the combustion of the extinguishing agent is less effective and the formation of COF₂ is preferred before HF.

It can be concluded that for all the tested extinguishing agents it is important to have an application system where the amount of agent is large enough to extinguish the fire fast and to ensure that the agent is well distributed through out the fire area. If this is achieved the amount of troublesome combustion products will be minimised.

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ANNEX A

Production of CO and CO₂ in tests with HFC125

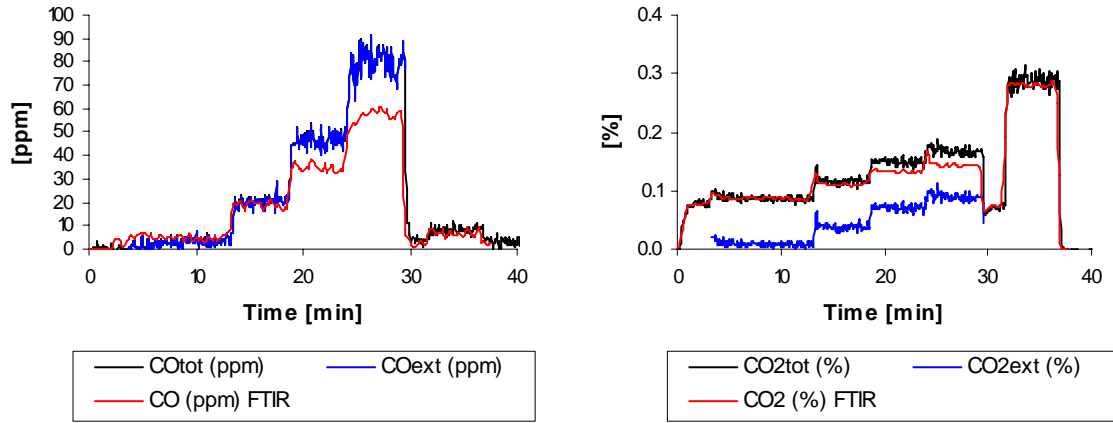


Figure A 1. Production of CO and CO₂ as a function of time from test 1 with HFC 125.

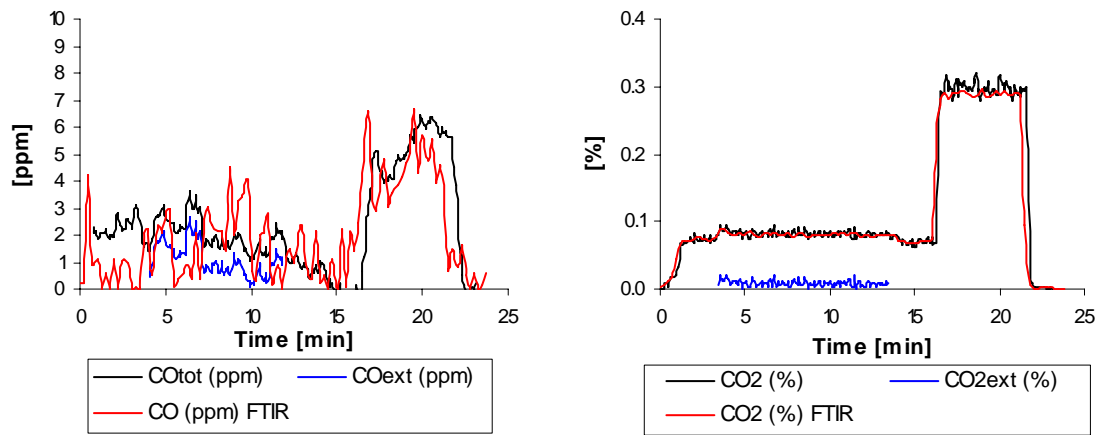


Figure A 2. Production of CO and CO₂ as a function of time from test 2 with HFC 125.

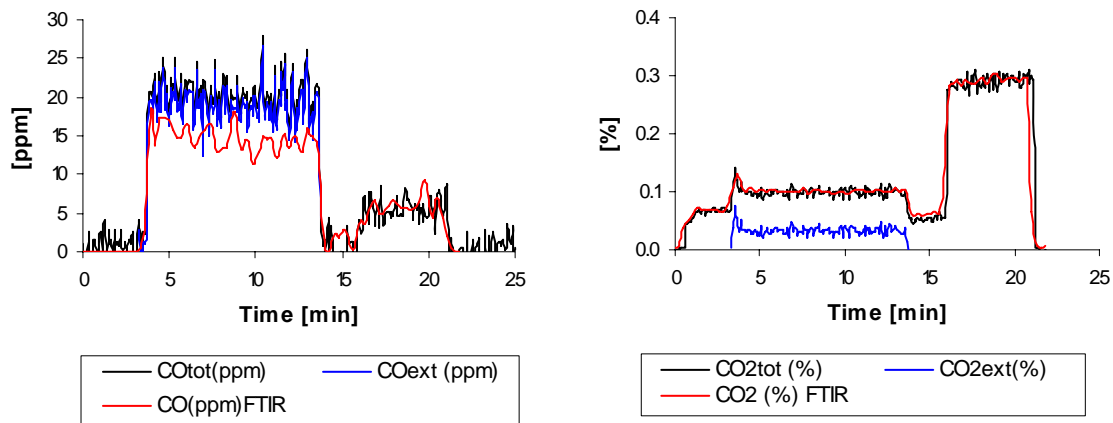


Figure A 3. Production of CO and CO₂ as a function of time from test 3 with HFC 125.

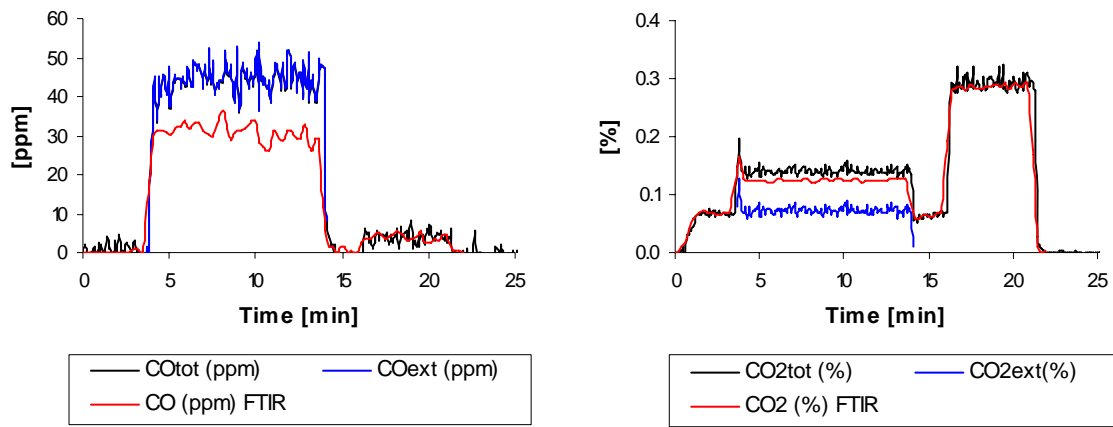


Figure A 4. Production of CO and CO₂ as a function of time from test 4 with HFC 125.

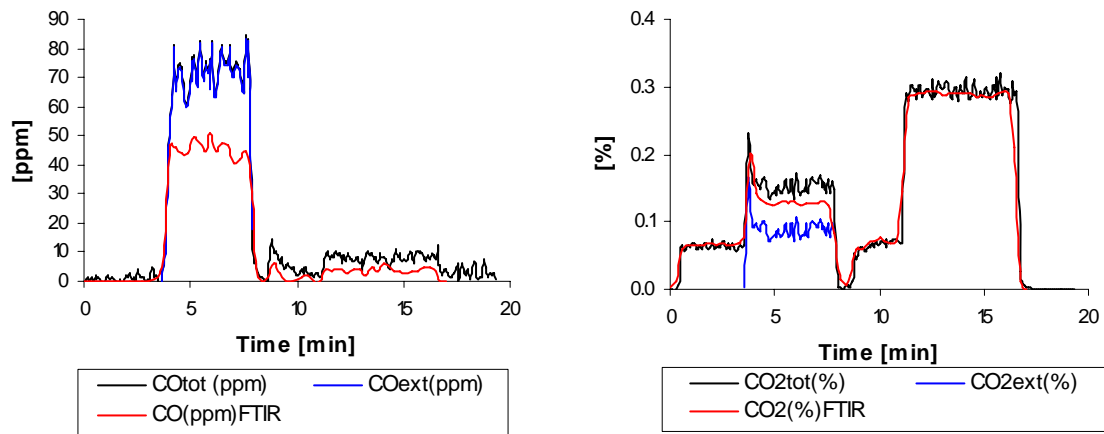
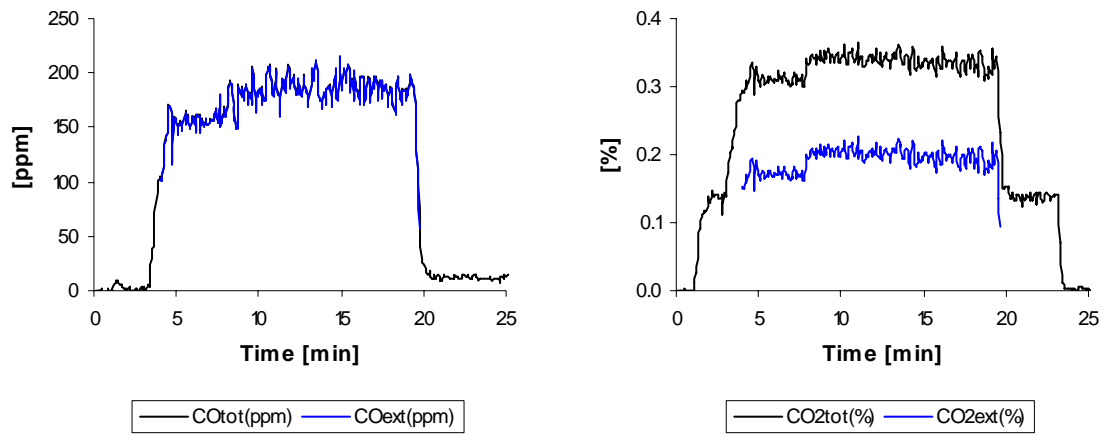
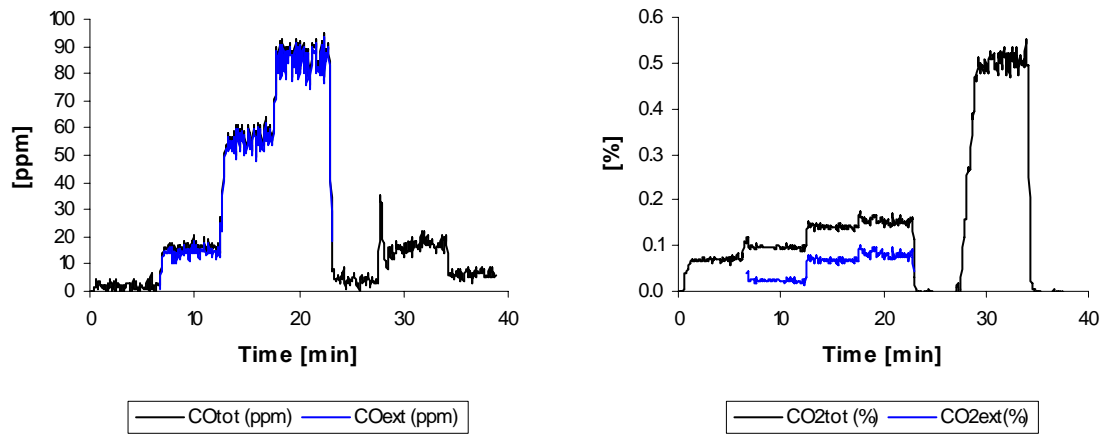
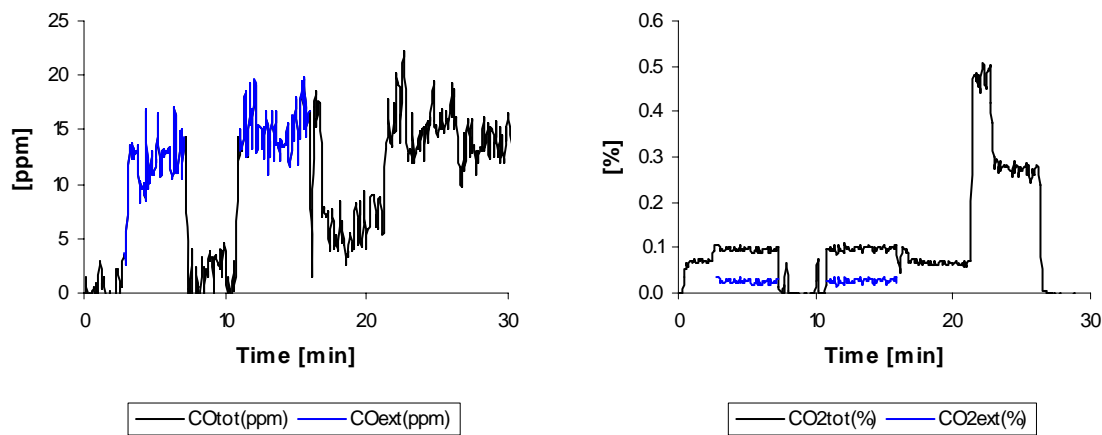


Figure A 5. Production of CO and CO₂ as a function of time from test 5 with HFC 125.

Production of CO and CO₂ in tests with HFC227eaFigure A 6. Production of CO and CO₂ as a function of time from test 1 with HFC 227ea.Figure A 7. Production of CO and CO₂ as a function of time from test 2 with HFC 227ea.Figure A 8. Production of CO and CO₂ as a function of time from test 3 with HFC 227ea.

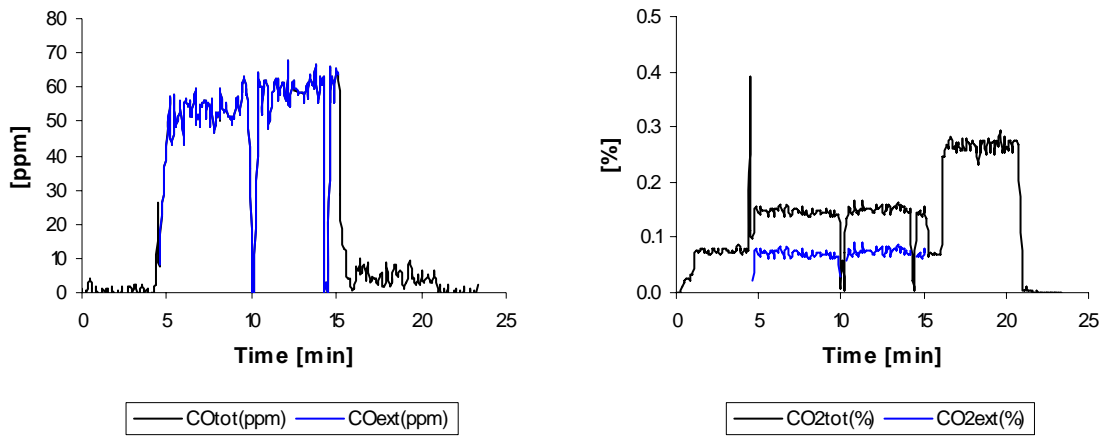


Figure A 9. Production of CO and CO₂ as a function of time from test 4 with HFC 227ea.

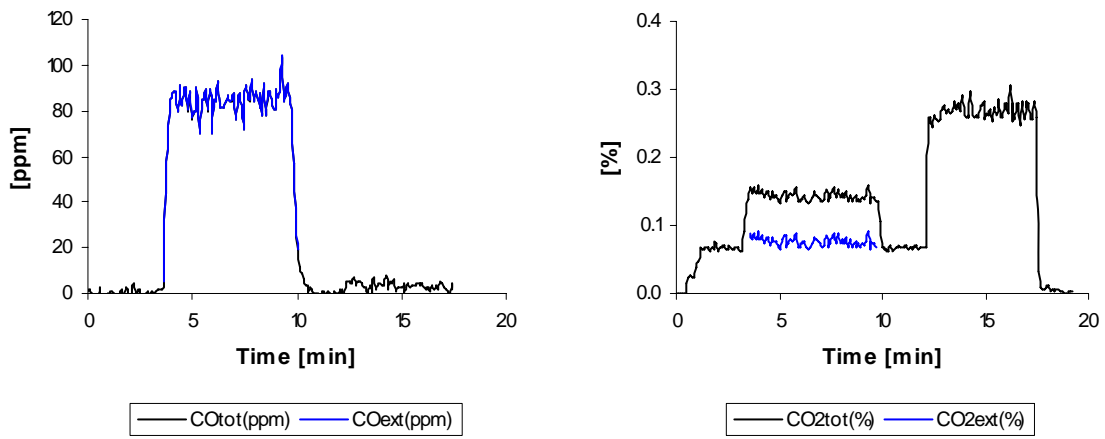


Figure A 10. Production of CO and CO₂ as a function of time from test 5 with HFC 227ea.

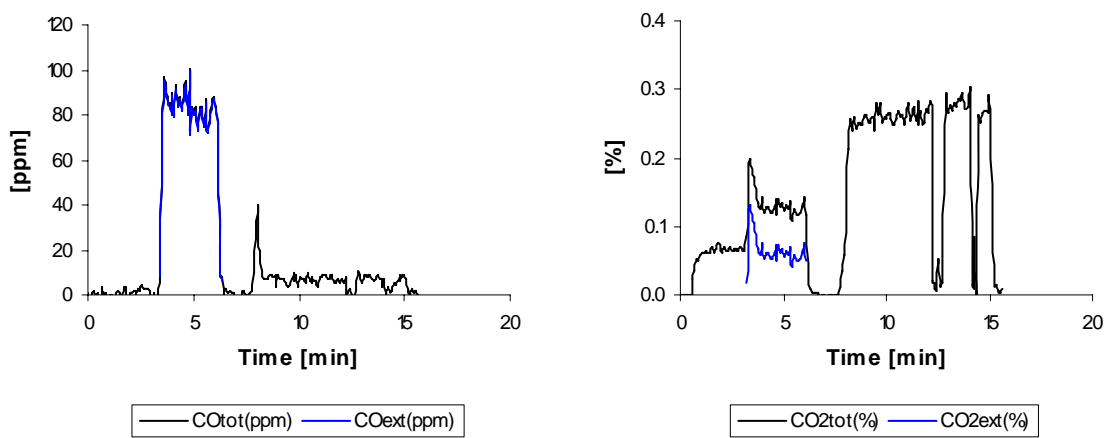


Figure A 11. Production of CO and CO₂ as a function of time from test 6 with HFC 227ea.

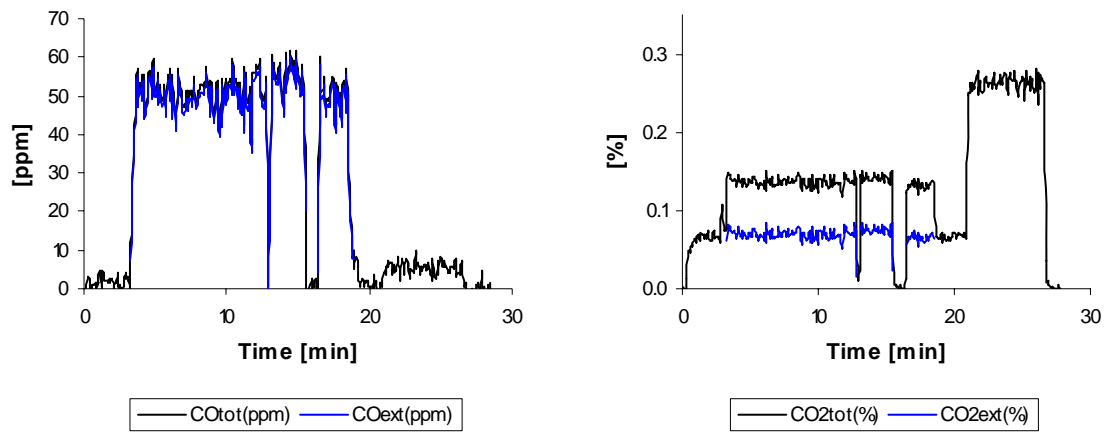


Figure A 12. Production of CO and CO₂ as a function of time from test 7 with HFC 227ea.

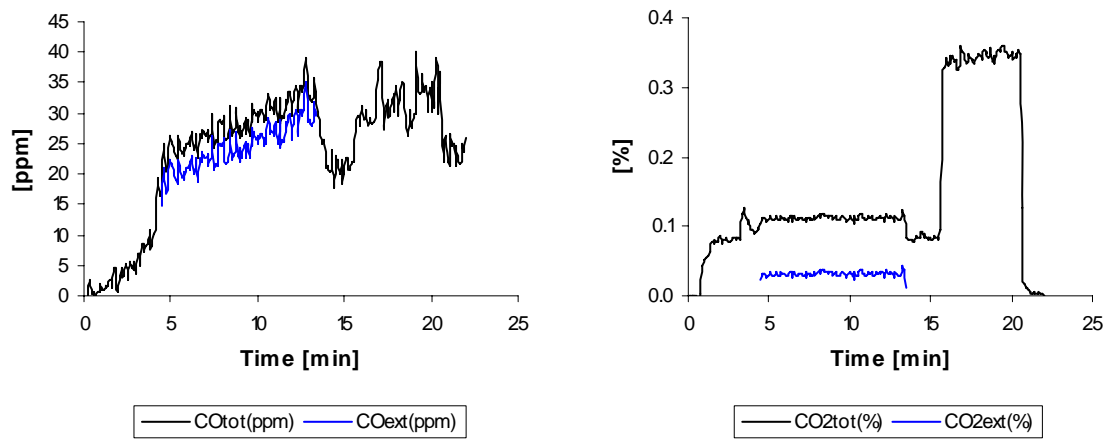


Figure A 13. Production of CO and CO₂ as a function of time from test F1 with HFC 227ea.

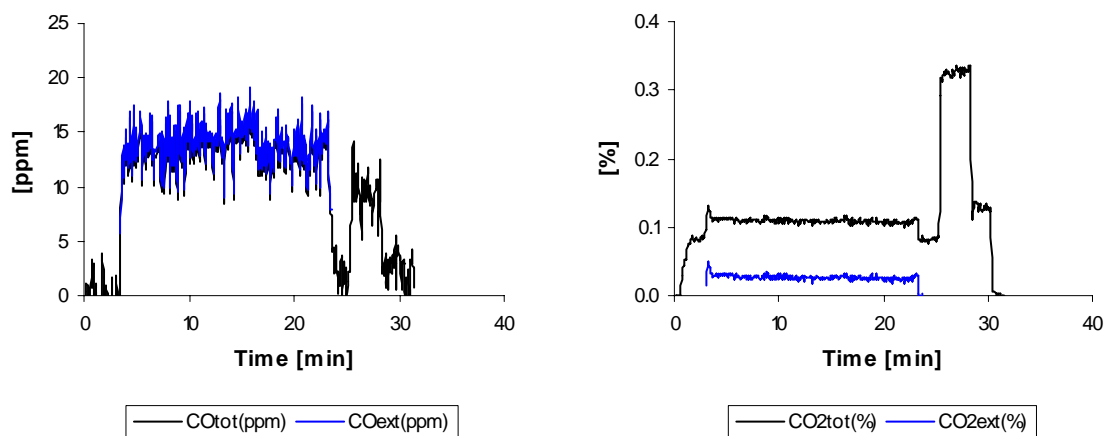


Figure A 14. Production of CO and CO₂ as a function of time from test F2 with HFC 227ea.

Production of CO and CO₂ in tests with C₆F-ketone.

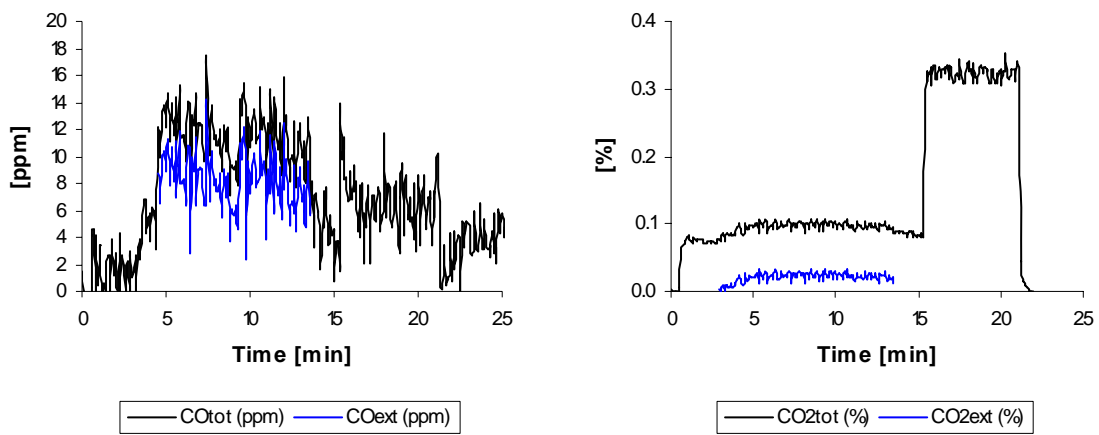


Figure A 15. Production of CO and CO₂ as a function of time from test 1 with C₆F-ketone.

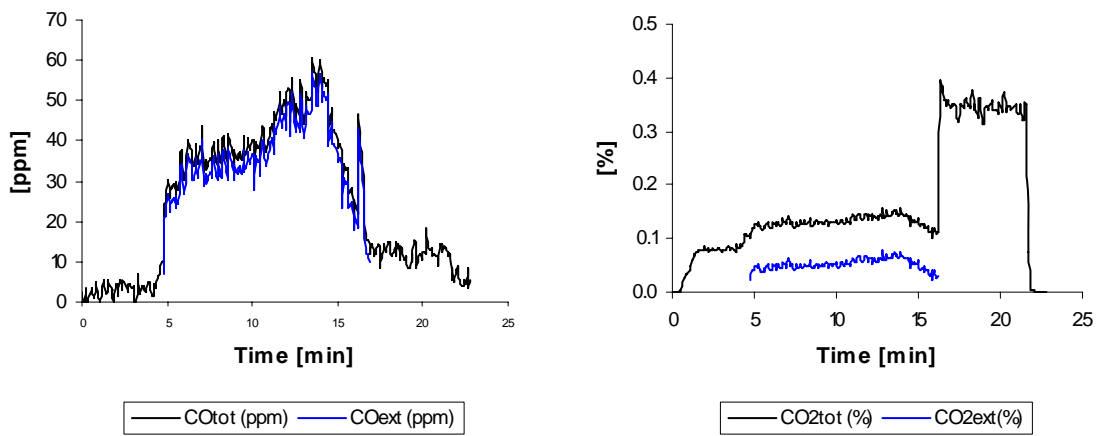


Figure A 16. Production of CO and CO₂ as a function of time from test 2 with C₆F-ketone.

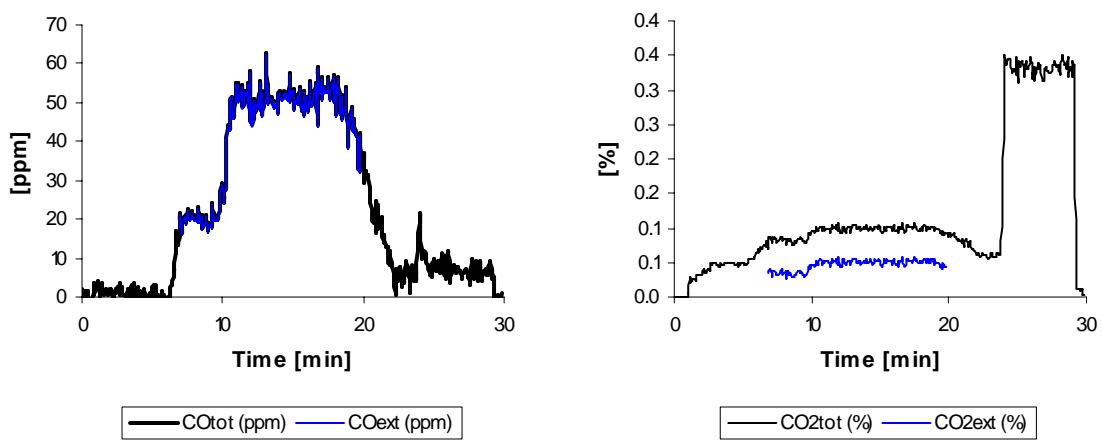


Figure A 17. Production of CO and CO₂ as a function of time from test 3 with C₆F-ketone.

Production of CO and CO₂ in tests with Halon 1301.

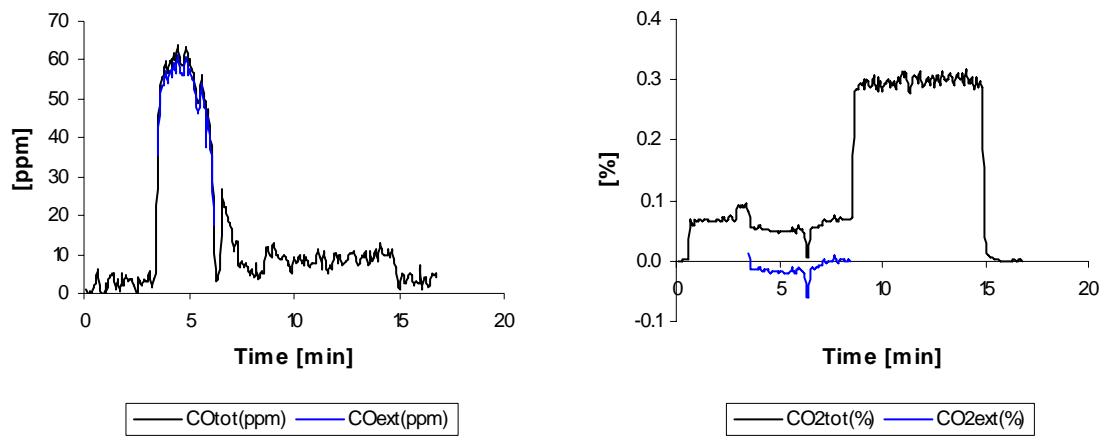


Figure A 18. Production of CO and CO₂ as a function of time from test 1 with Halon 1301.

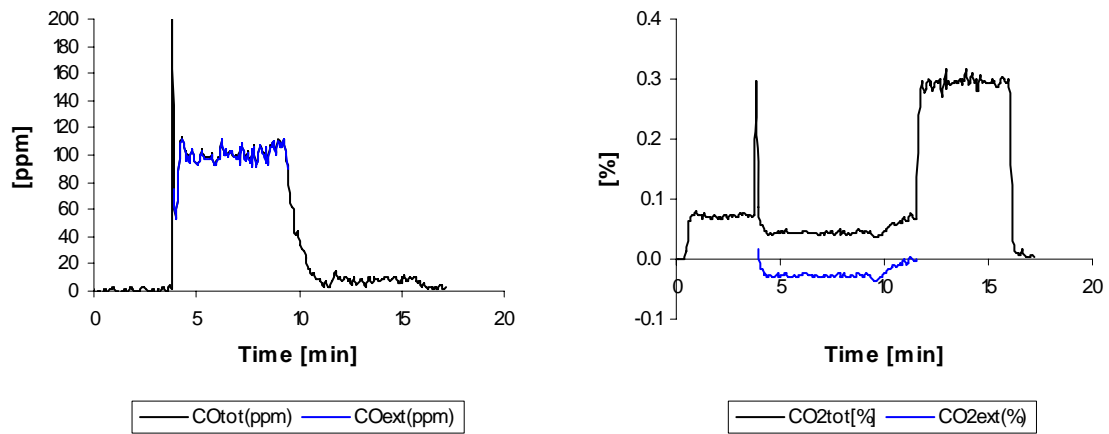


Figure A 19. Production of CO and CO₂ as a function of time from test 2 with Halon 1301.

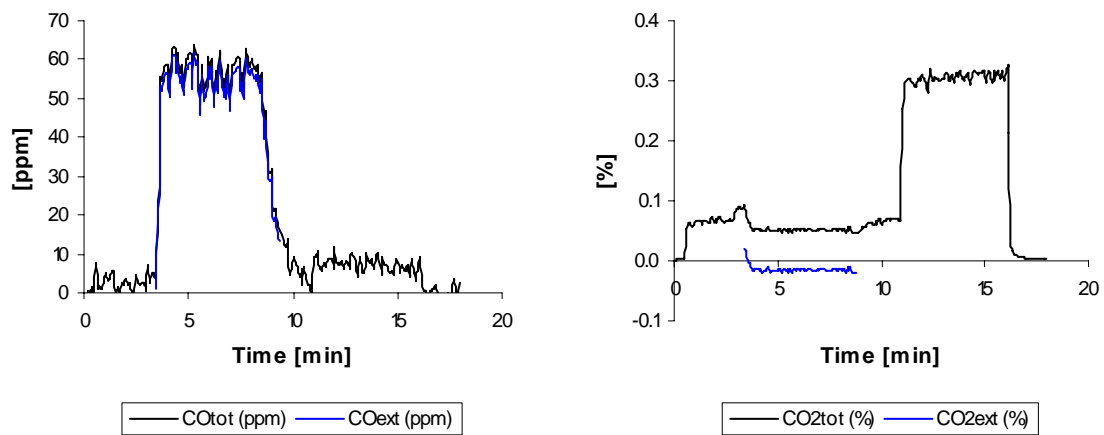


Figure A 20. Production of CO and CO₂ as a function of time from test 3 with Halon 1301.

ANNEX B

Extinction coefficient, K, in tests with HFC125

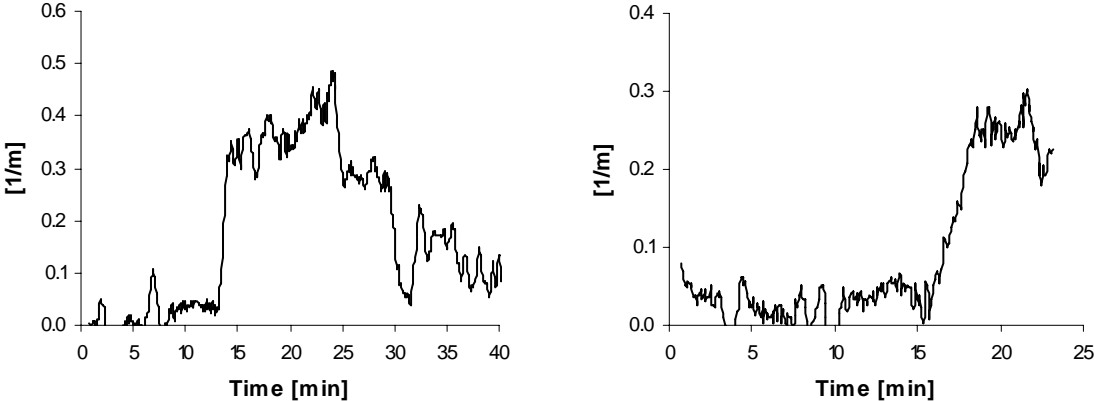


Figure B 1. Extinction coefficient, K, as a function of time for tests 1 and 2 with HFC125.

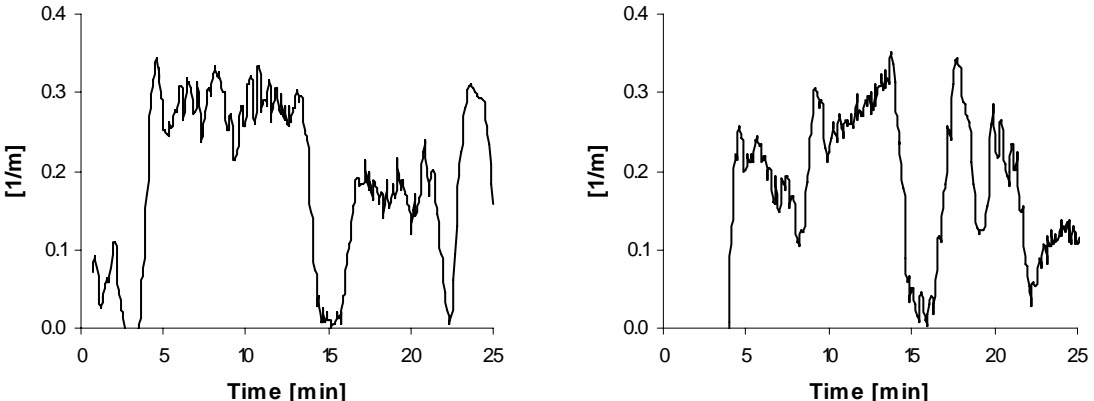


Figure B 2. Extinction coefficient, K, as a function of time for tests 3 and 4 with HFC125.

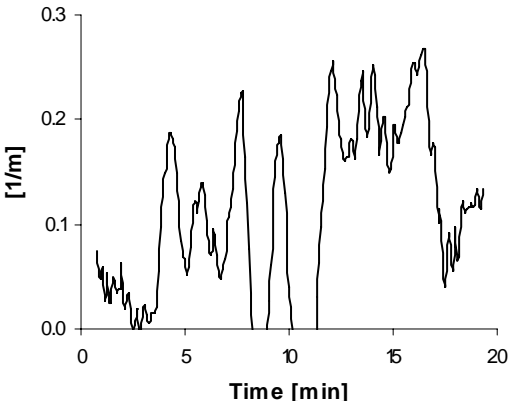


Figure B 3. Extinction coefficient, K, as a function of time for test 5 with HFC125.

Extinction coefficient, K , in tests with HFC227ea

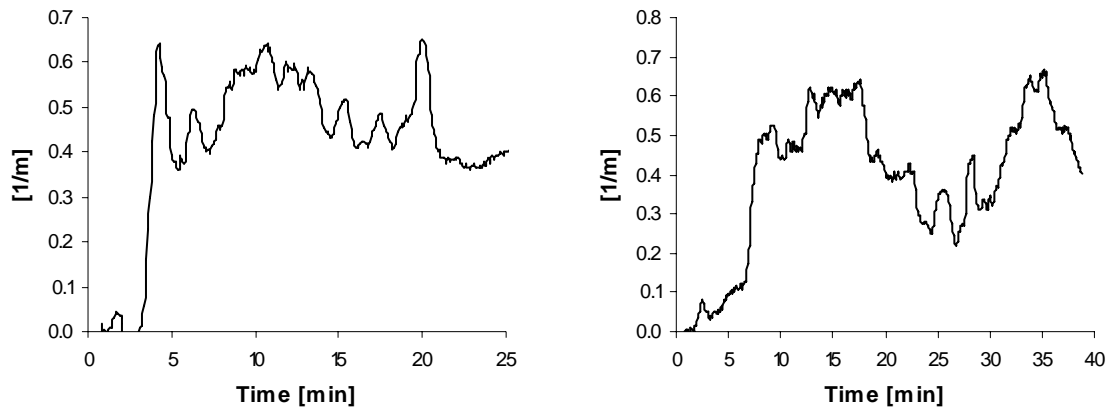


Figure B 4. Extinction coefficient, K , as a function of time for tests 1 and 2 with HFC227ea.

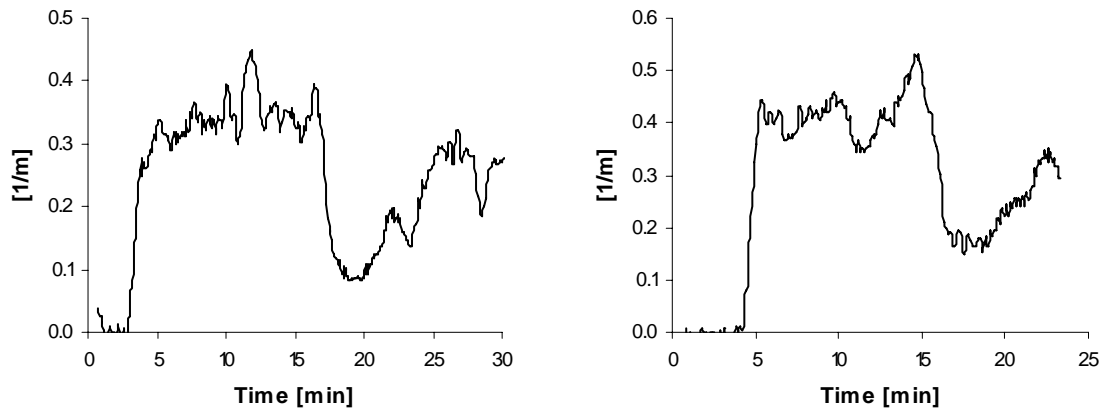


Figure B 5. Extinction coefficient, K , as a function of time for tests 3 and 4 with HFC227ea.

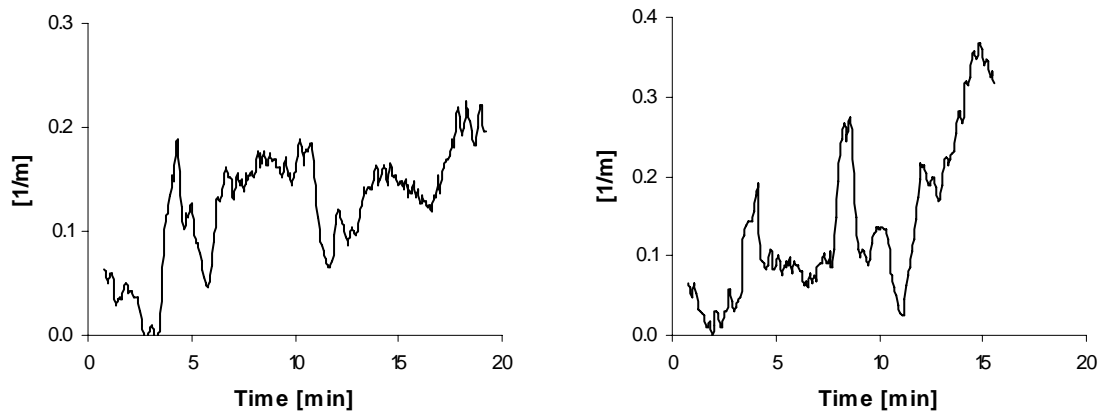


Figure B 6. Extinction coefficient, K , as a function of time for tests 5 and 6 with HFC227ea.

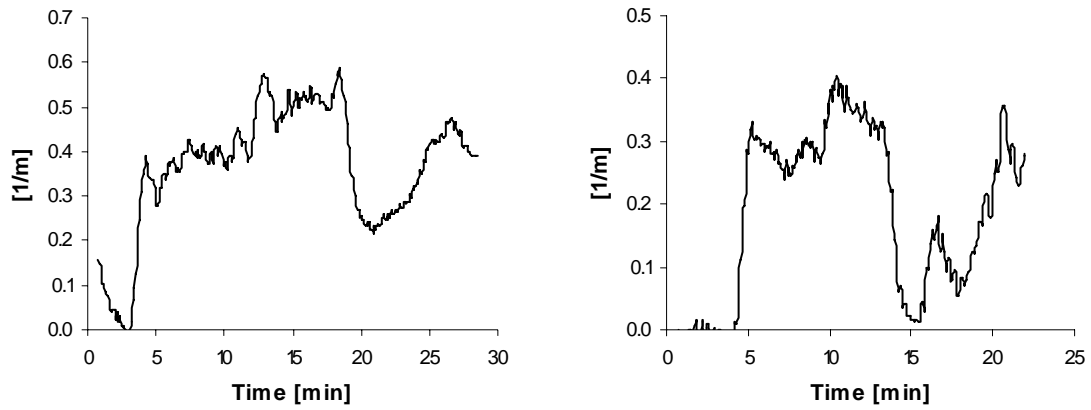


Figure B 7. Extinction coefficient, K , as a function of time for tests 7 and F1 with HFC227ea.

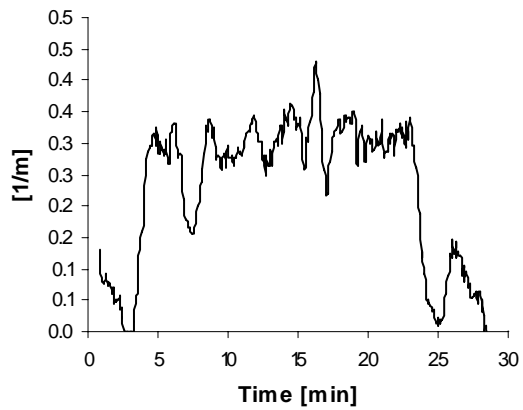


Figure B 8. Extinction coefficient, K , as a function of time for test F2 with HFC227ea.

Extinction coefficient, K , in tests with C_6F_{12} -ketone

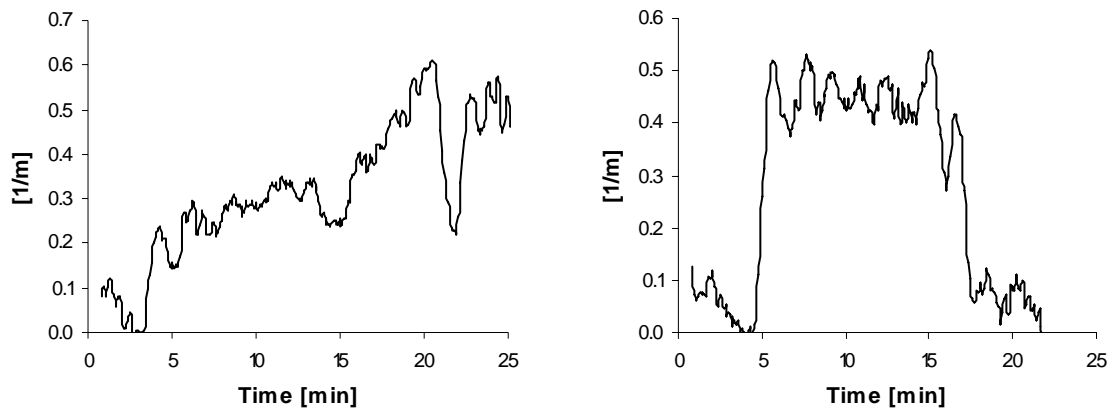


Figure B 9. Extinction coefficient, K , as a function of time for tests 1 and 2 with C_6F_{12} -ketone.

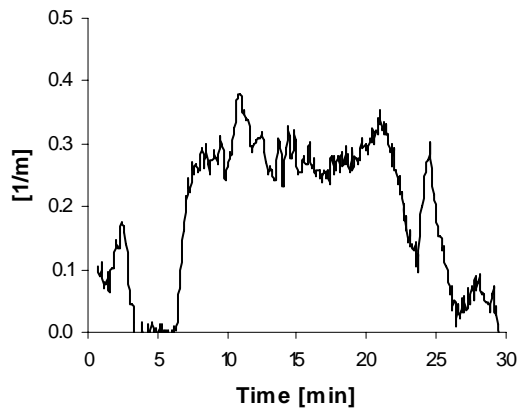
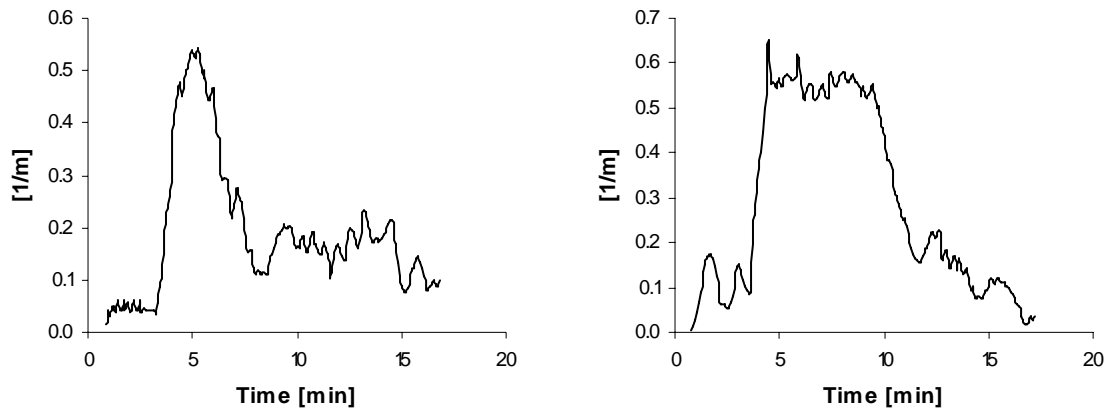
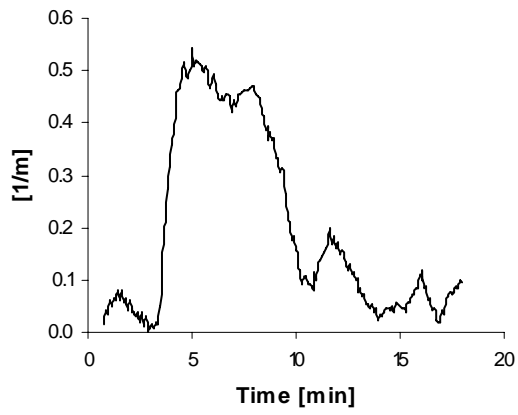


Figure B 10 Extinction coefficient, K , as a function of time for test 3 with C_6F_{12} -ketone.

Extinction coefficient, K , in tests with Halon 1301Figure B 11. Extinction coefficient, K , as a function of time for tests 1 and 2 with Halon 1301.Figure B 12. Extinction coefficient, K , as a function of time for test 3 with Halon 1301.

ANNEX C

Table C 1. Results on fluorine containing combustion products from HFC 227ea.

Extinction agent (%-REMP)	Test ID	HF g/g agent	HF % F from agent as HF	COF₂ g/g agent	COF₂ % F from agent as COF₂
24	227_3	0.6	72.7	0.016	1.2
	227_F1	0.72	88	0.027	2
	227_F2	0.73	89.2	0.024	1.8
65	227_4	0.33	40.3	0.074	5.5
	227_7	0.31	37.2	0.063	4.6
91	227_2*	0.21	25.5	0.049	3.6
	227_5	0.24	28.7	0.13	9.6
100	227_6	0.19	23.5	0.13	9.9
	227_2*	0.17	21.1	0.1	7.6

* The results on HF and COF₂ from 24 %- and 65 %- extinction agent in test 227_2 were very low and were regarded as outliers.

Table C 2. Results on other combustion products from HFC 227ea.

Extinction agent (%-REMP)	Test ID	CO g/g agent	HBr g/g agent	HBr % Br from agent as HBr
24	227_3	0.018	-	-
	227_F1	0.025	-	-
	227_F2	0.025	-	-
65	227_4	0.031	-	-
	227_7	0.028	-	-
91	227_2	0.019	-	-
	227_5	0.035	-	-
100	227_6	0.033	-	-
	227_2	0.023	-	-

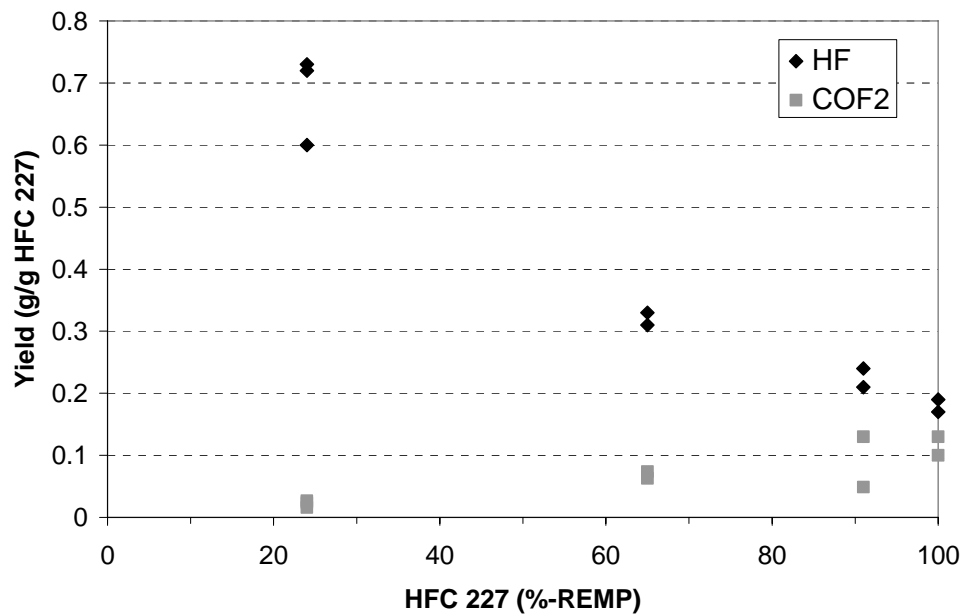


Figure C 1. Yields of fluorine containing combustion products from HFC 227ea.

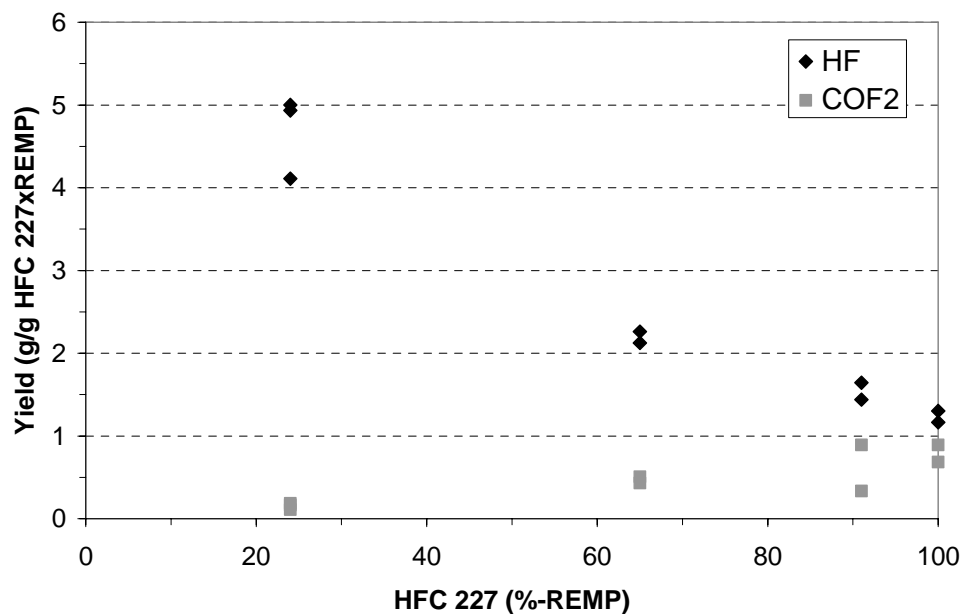


Figure C 2. Normalized yields (REMP = 6.8) of fluorine containing combustion products from HFC 227ea.

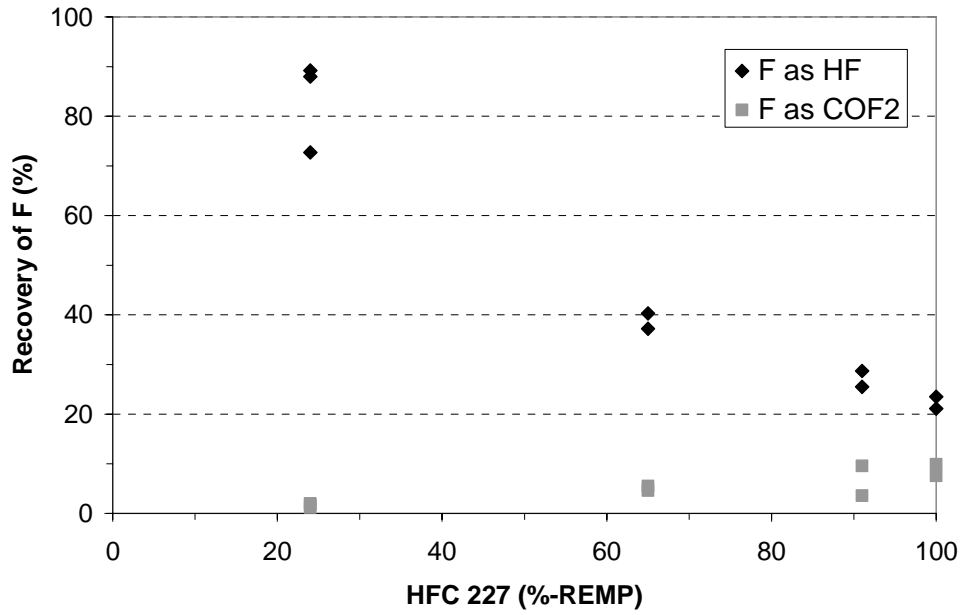


Figure C 3. Recoveries of fluorine from HFC 227ea as HF and COF₂, respectively.

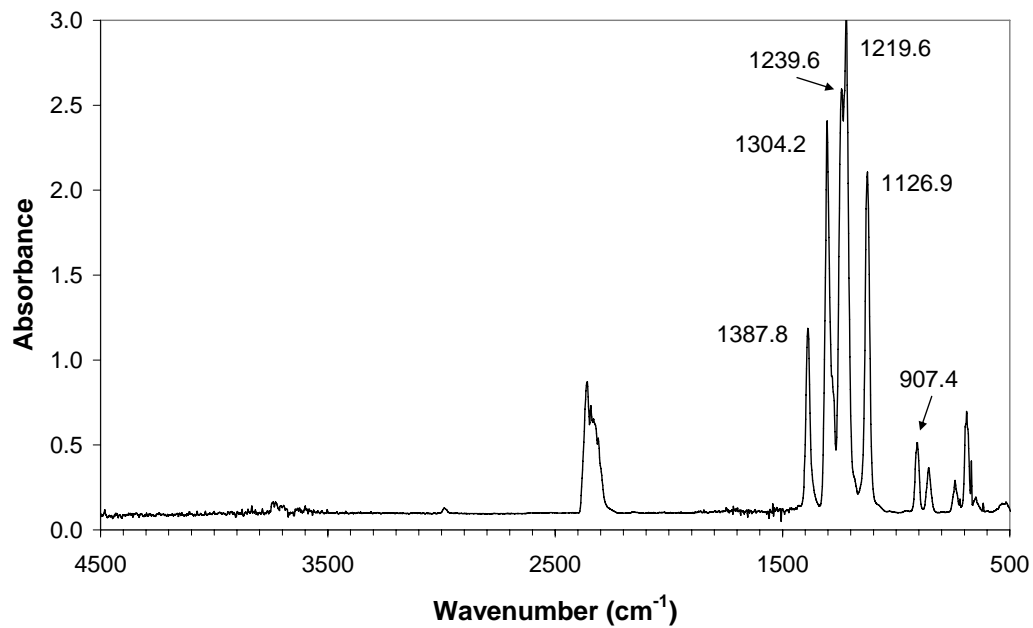


Figure C 4. FTIR spectrum on approx. 640 ppm HFC 227ea.

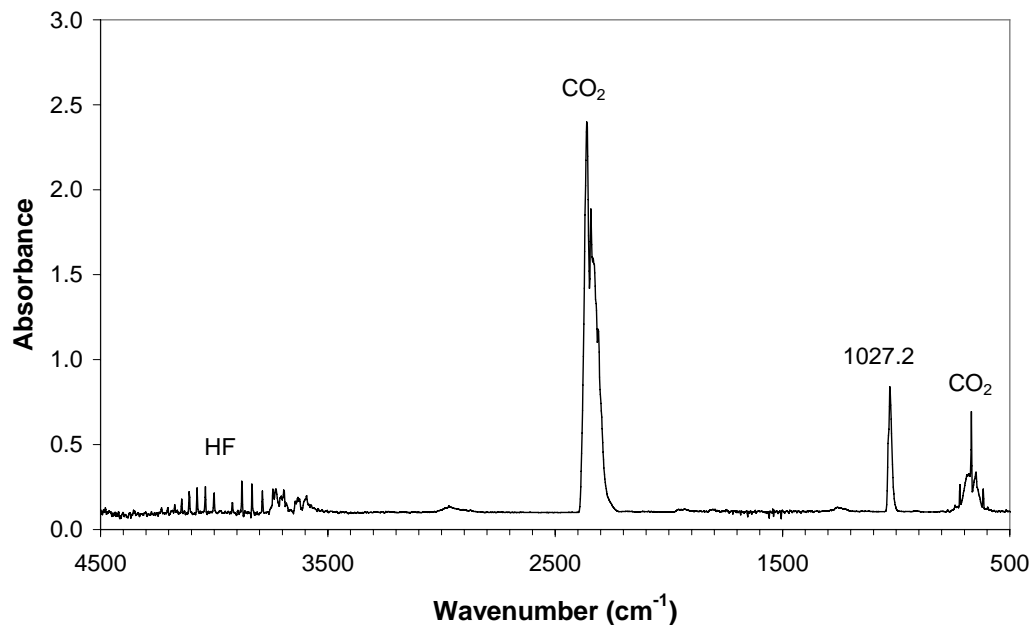


Figure C 5. FTIR spectrum from test with 24 % HFC 227ea (24 % of extinguishment concentration, REMP).

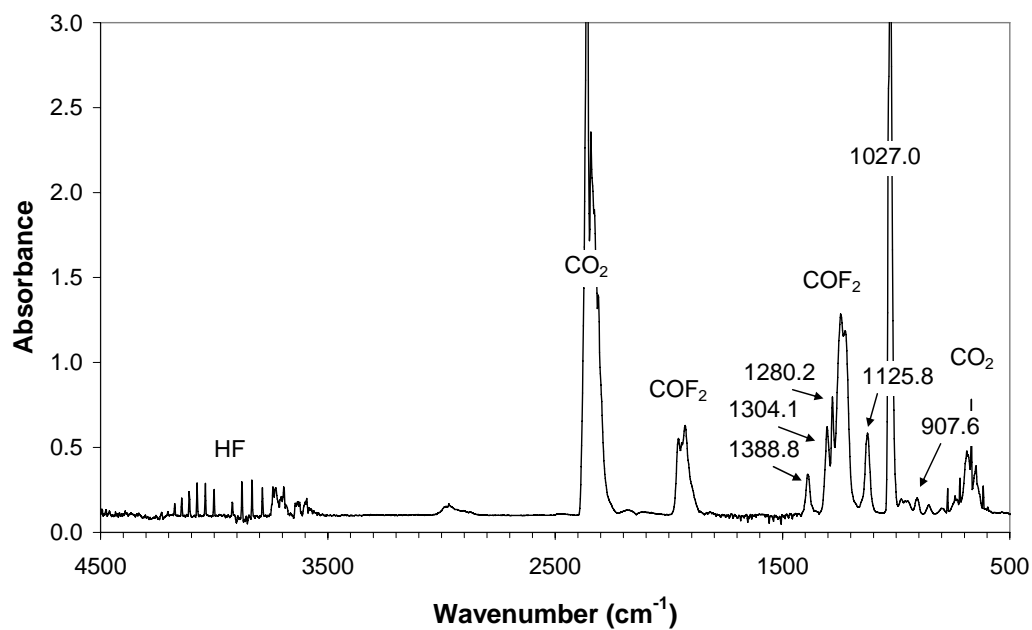


Figure C 6. FTIR spectrum from test with 91 % HFC 227ea.

Table C 3. Results on fluorine containing combustion products from HFC 125.

Extinction agent (%-REMP)	Test ID	HF g/g agent	HF % F from agent as HF	COF₂ g/g agent	COF₂ % F from agent as COF₂
10	125_1	0.64	76.5	< 0.01	< 0.5
	125_2	0.73	87.1	< 0.01	< 0.5
37	125_1	0.48	57.4	0.044	3.2
	125_3	0.51	60.9	0.049	3.6
	125_6	0.49	58.8	0.033	2.39
67	125_1	0.33	39.2	0.082	5.9
	125_4	0.33	40.2	0.081	5.9
82	125_1	0.25	30	0.12	8.5
86	125_5	0.27	32.4	0.15	10.8

Table C 4. Results on other combustion products from HFC 125.

Extinction agent (%-REMP)	Test ID	CO g/g agent	HBr g/g agent	HBr % Br from agent as HBr
10	125_1	0.025	-	-
	125_2	< 0.01	-	-
37	125_1	0.026	-	-
	125_3	0.020	-	-
	125_6	0.17	-	-
67	125_1	0.027	-	-
	125_4	0.023	-	-
82	125_1	0.032	-	-
86	125_5	0.026	-	-

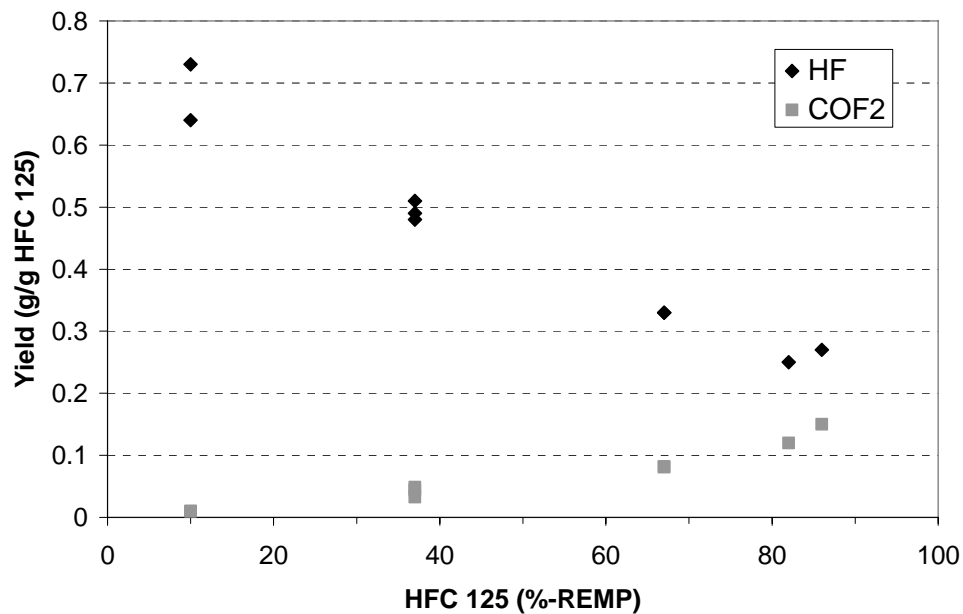


Figure C 7. Yields of fluorine containing combustion products from HFC 125.

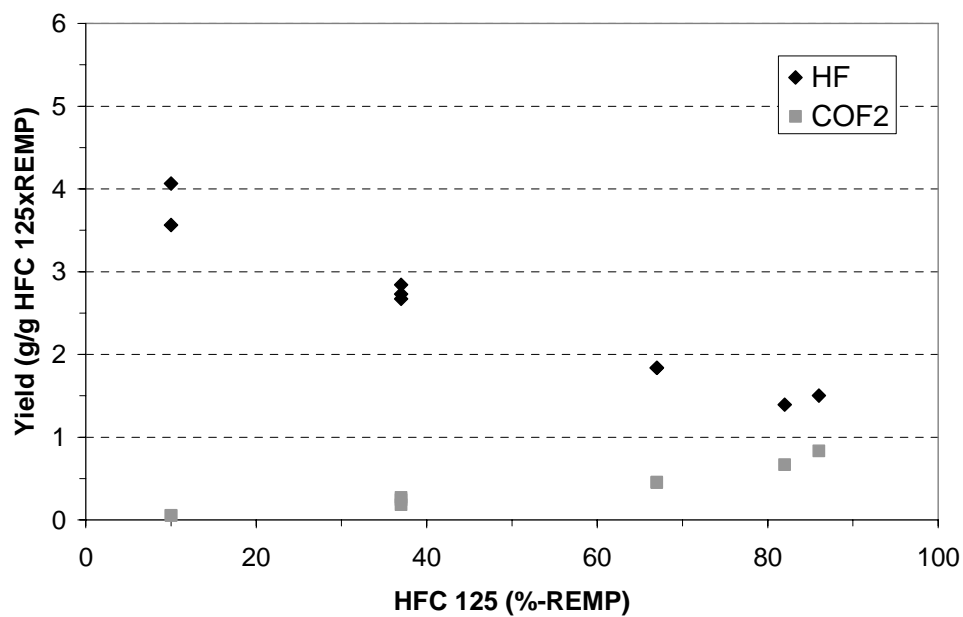


Figure C 8. Normalized yields (REMP = 5.6) of fluorine containing combustion products from HFC 125.

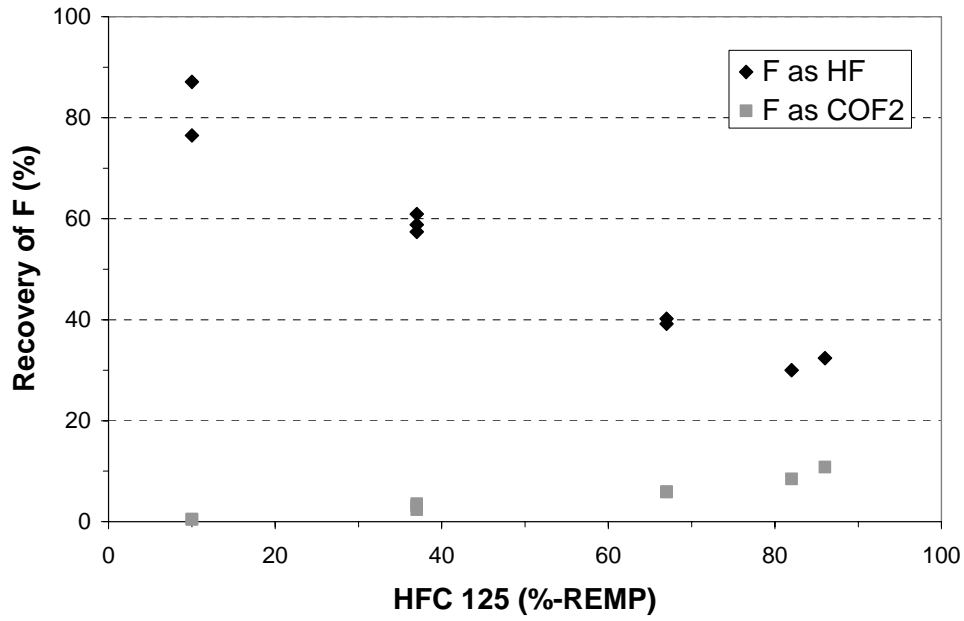


Figure C 9. Recoveries of fluorine from HFC 125 as HF and COF₂, respectively.

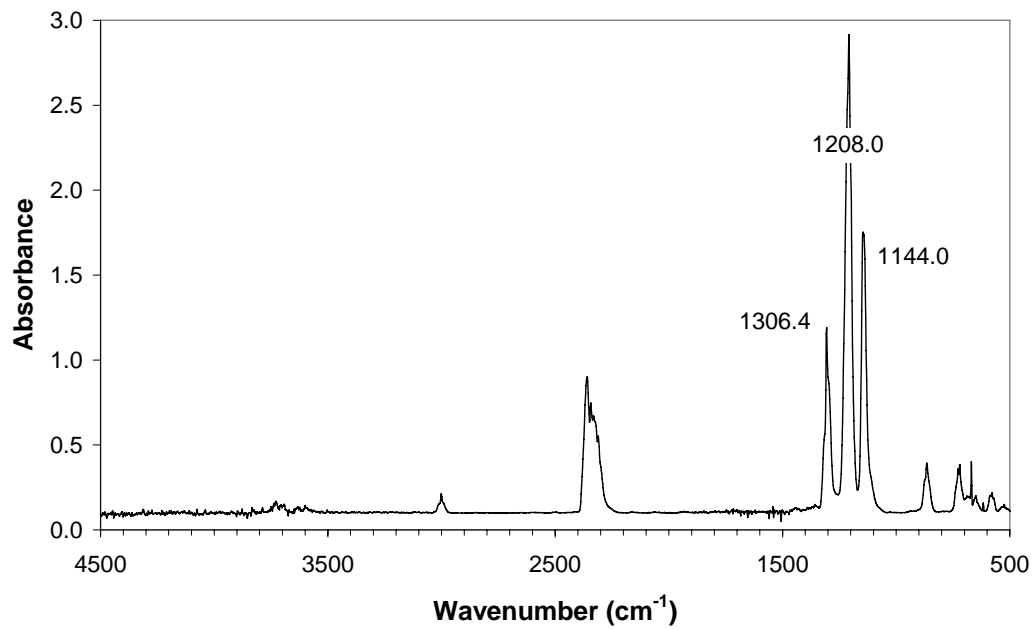


Figure C 10. FTIR spectrum on approx. 250 ppm HFC 125.

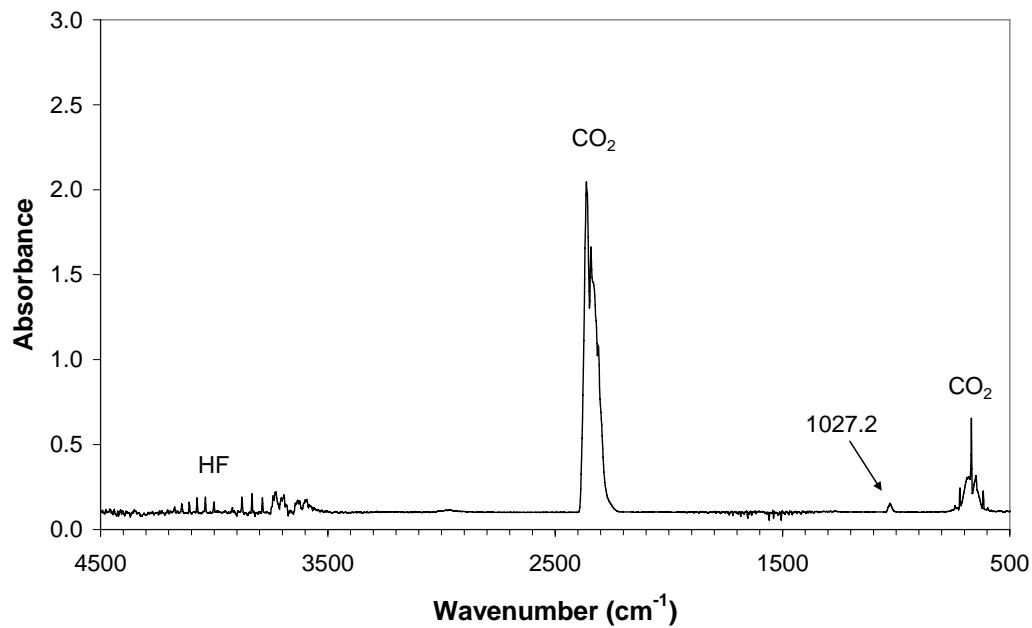


Figure C 11. FTIR spectrum from test with 10 % HFC 125.

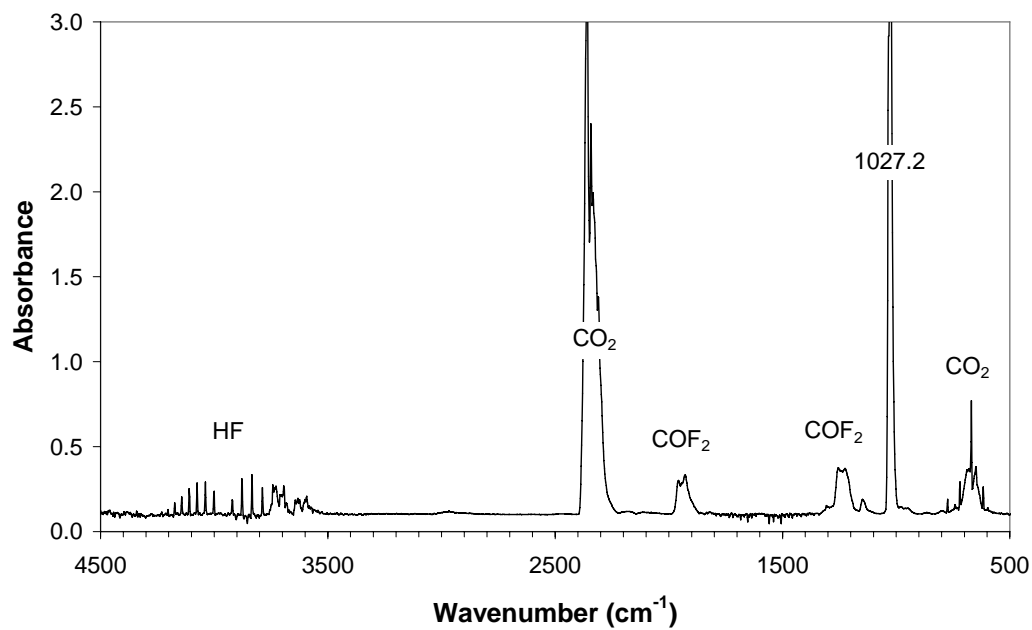


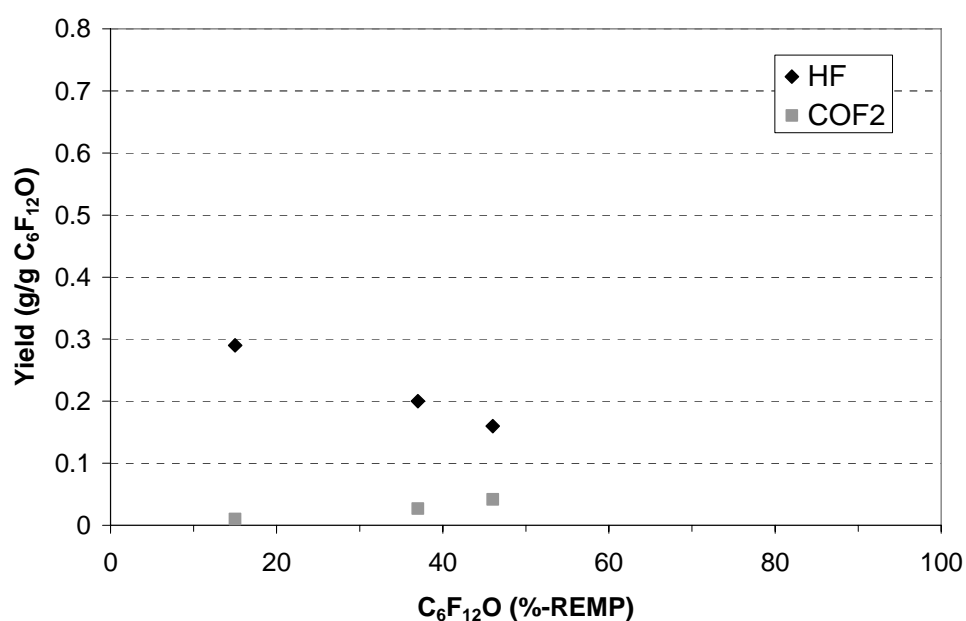
Figure C 12. FTIR spectrum from test with 67 % HFC 125.

Table C 5. Results on fluorine containing combustion products from C₆F₁₂-ketone.

Extinction agent (%-REMP)	Test ID	HF g/g agent	HF % F from agent as HF	COF ₂ g/g agent	COF ₂ % F from agent as COF ₂
15	C ₆ F ₁₂ -ketone_1	0.29	38.2	< 0.01	23.1
37	C ₆ F ₁₂ -ketone_2	0.20	26.3	0.027	16.0
46	C ₆ F ₁₂ -ketone_3	0.16	21.1	0.042	12.8

Table C 6. Results on other combustion products from C₆F₁₂-ketone.

Extinction agent (%-REMP)	Test ID	CO g/g agent	HCl g/g agent	HBr g/g agent	HBr % Br from agent as HBr
15	C ₆ F ₁₂ -ketone_1	0.0145	0.014	-	-
37	C ₆ F ₁₂ -ketone_2	0.0146	0.035	-	-
46	C ₆ F ₁₂ -ketone_3	0.0161	< 0.01	-	-

**Figure C 13. Yields of fluorine containing combustion products from C₆F₁₂-ketone.**

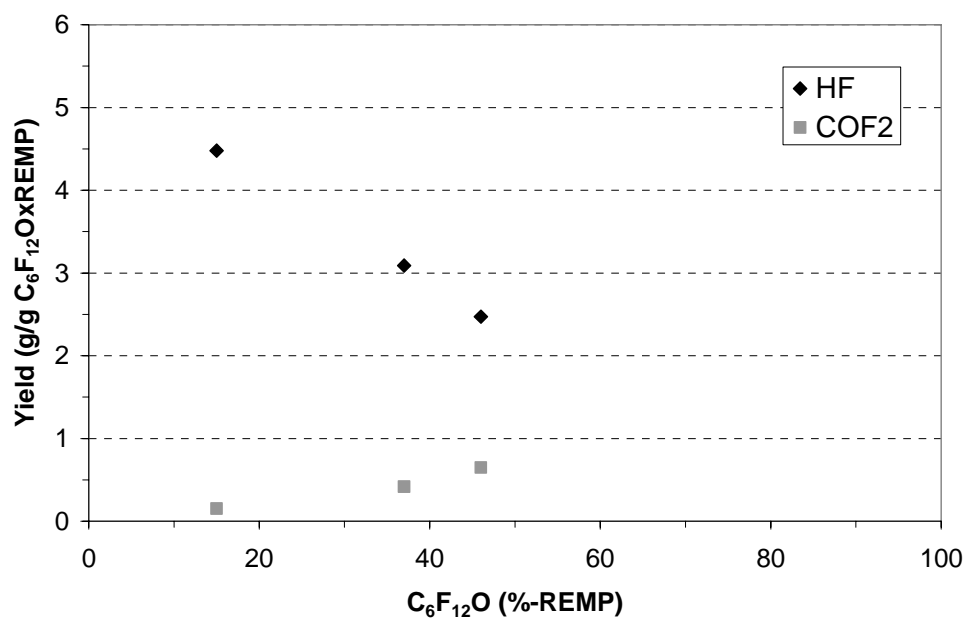


Figure C 14. Normalized yields (REMP = 15.4) of fluorine containing combustion products from C₆F₁₂-ketone.

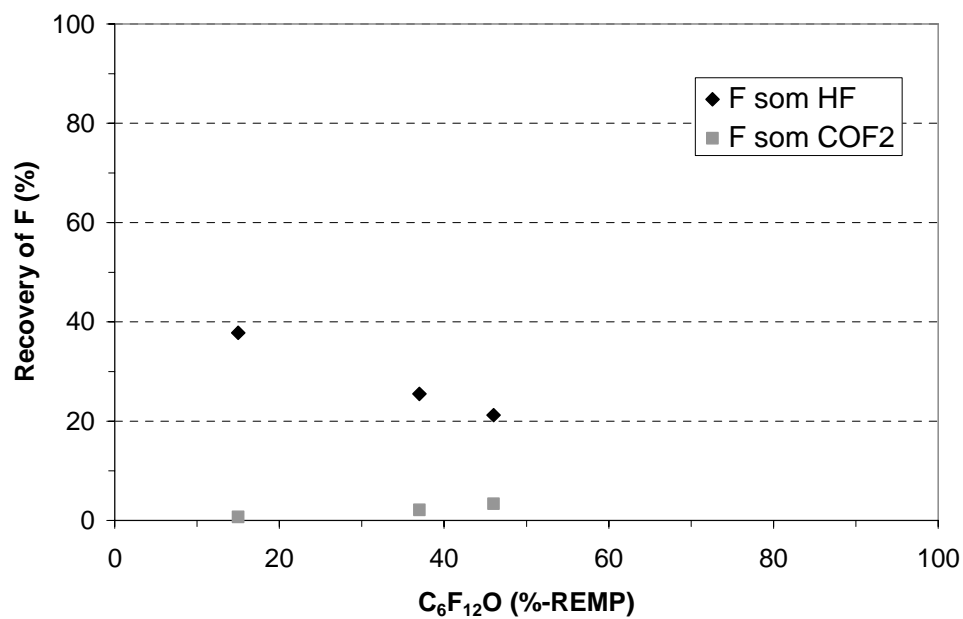


Figure C 15. Recoveries of fluorine from C₆F₁₂-ketone as HF and COF₂, respectively.

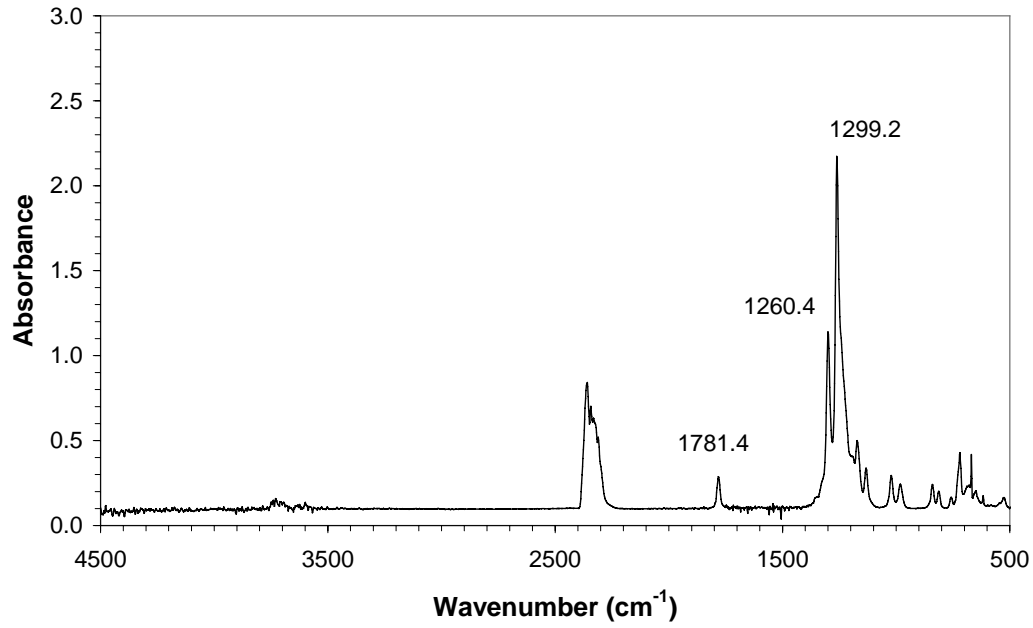


Figure C 16. FTIR spectrum for C₆F₁₂-ketone mixed in air.

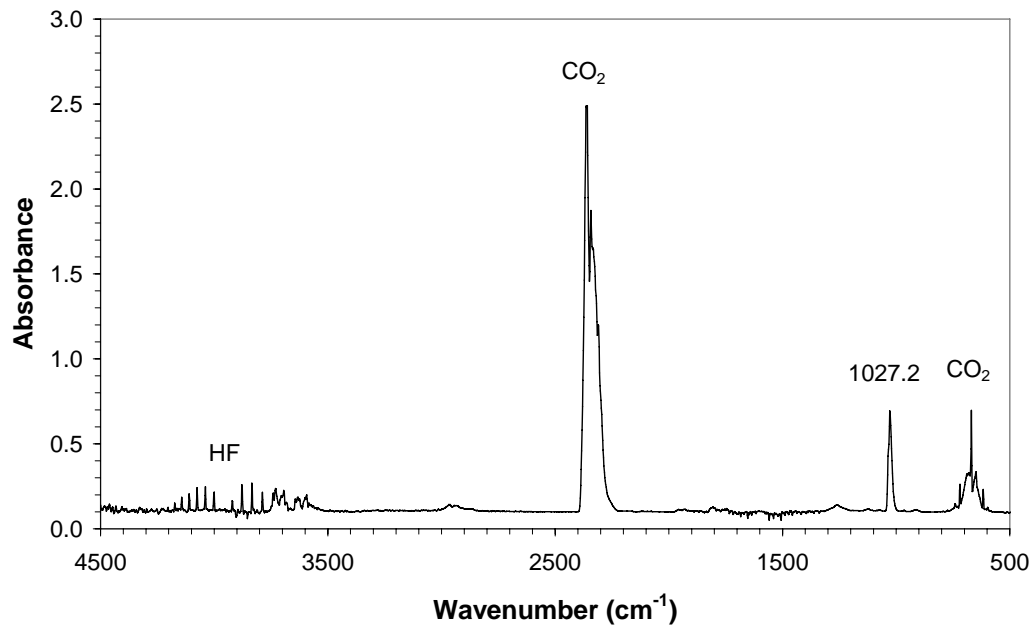


Figure C 17. FTIR spectrum from test with 15 % of C₆F₁₂-ketone.

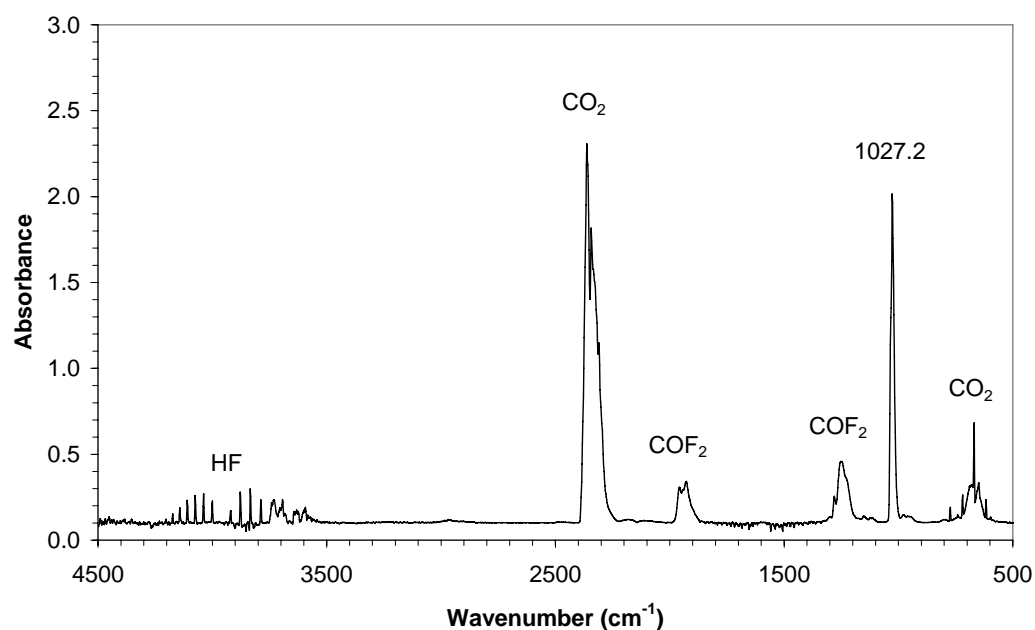
Figure C 18. FTIR spectrum from test with 47 % of C₆F₁₂-ketone.

Table C 7. Results on fluorine containing combustion products from halon 1301.

Extinction agent (%-REMP)	Test ID	HF g/g agent	HF % F from agent as HF	COF ₂ g/g agent	COF ₂ % F from agent as COF ₂
56	1301_3	0.37	90.4	0.019	2.8
86	1301_2	0.36	90.1	0.040	6.1

Table C 8. Results on other combustion products from halon 1301.

Extinction agent (%-REMP)	Test ID	CO g/g agent	HBr g/g agent	HBr % Br from agent as HBr
56	1301_3	0.20	0.39	70.9
86	1301_2	0.24	0.46	84.1

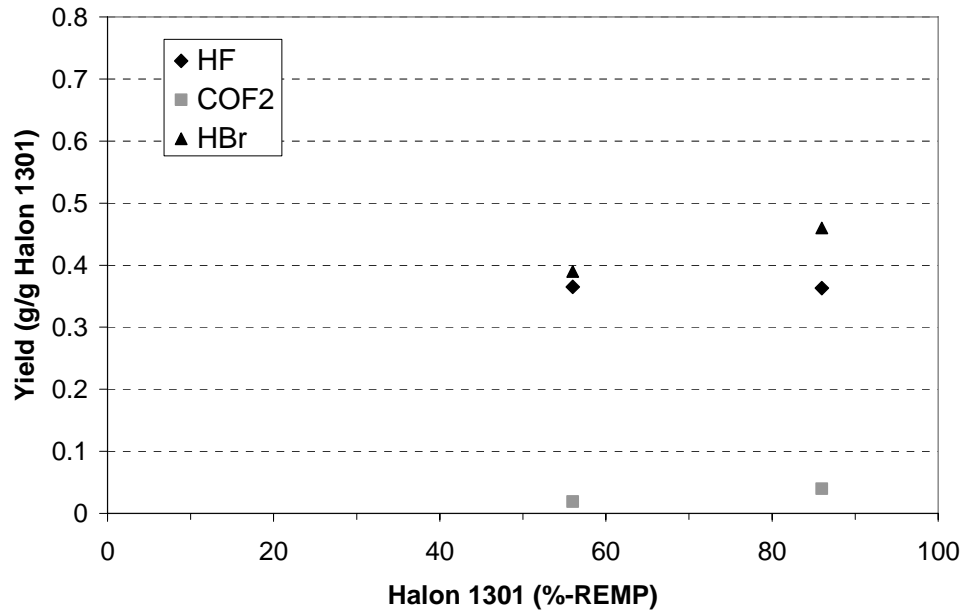


Figure C 19. Yields of fluorine and bromine containing combustion products from halon 1301.

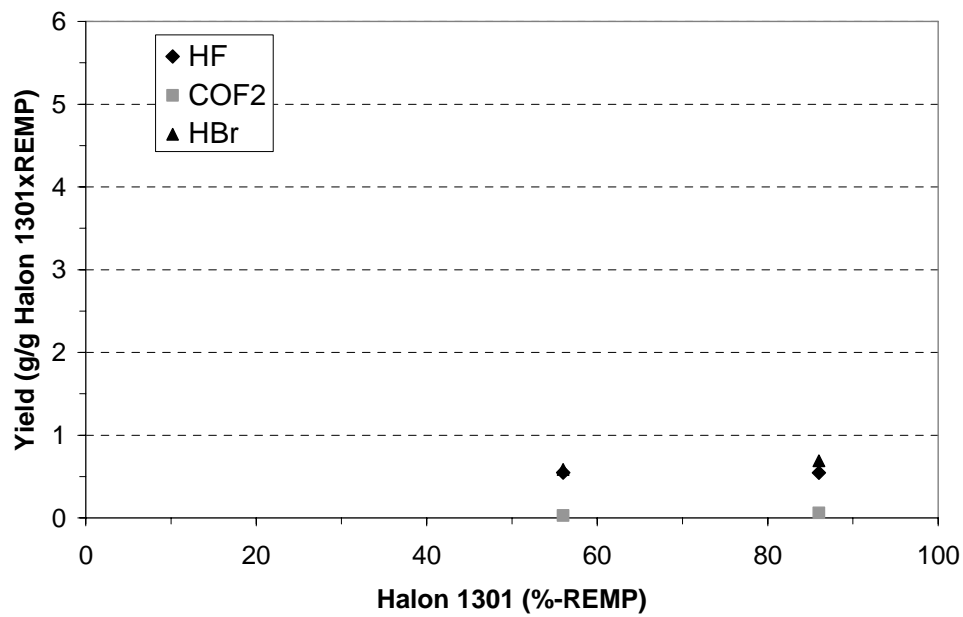


Figure C 20. Normalized yields (REMP = 1.5) of fluorine and bromine containing combustion products from halon 1301.

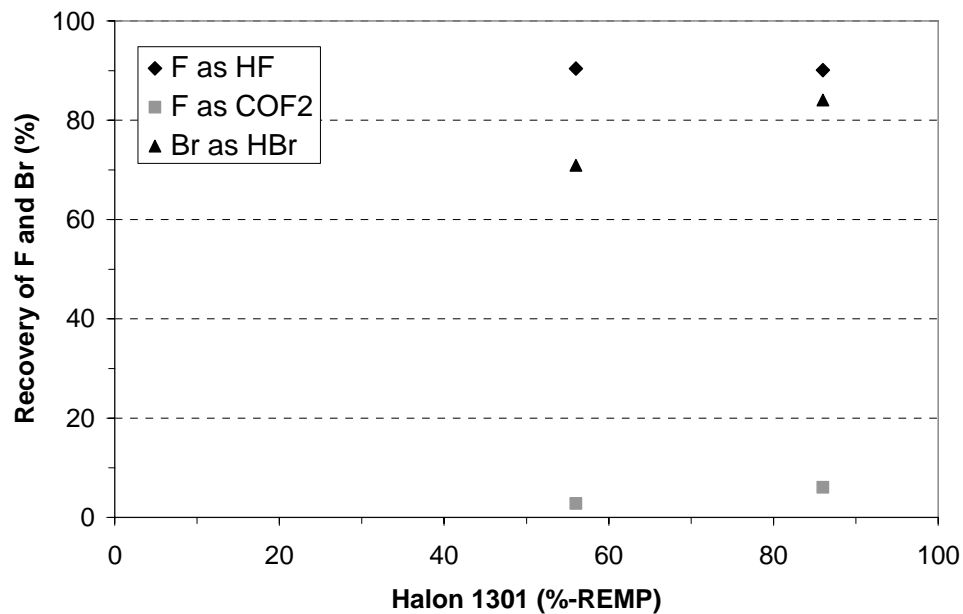


Figure C 21. Recoveries of fluorine and bromine from Halon 1301 as HF and COF₂, and HBr, respectively.

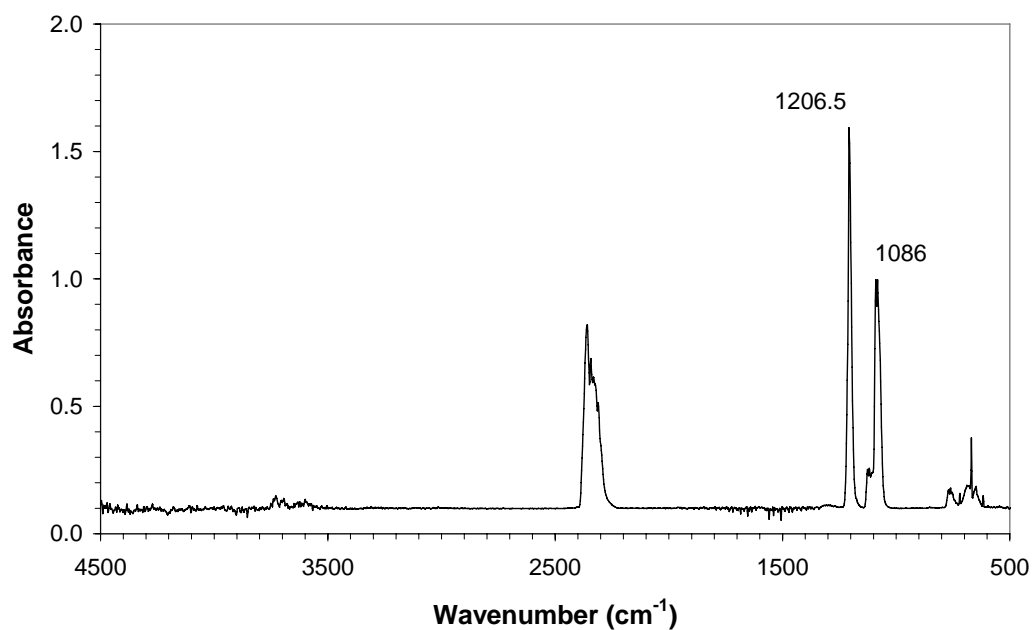


Figure C 22. FTIR spectrum for Halon 1301 mixed in air.

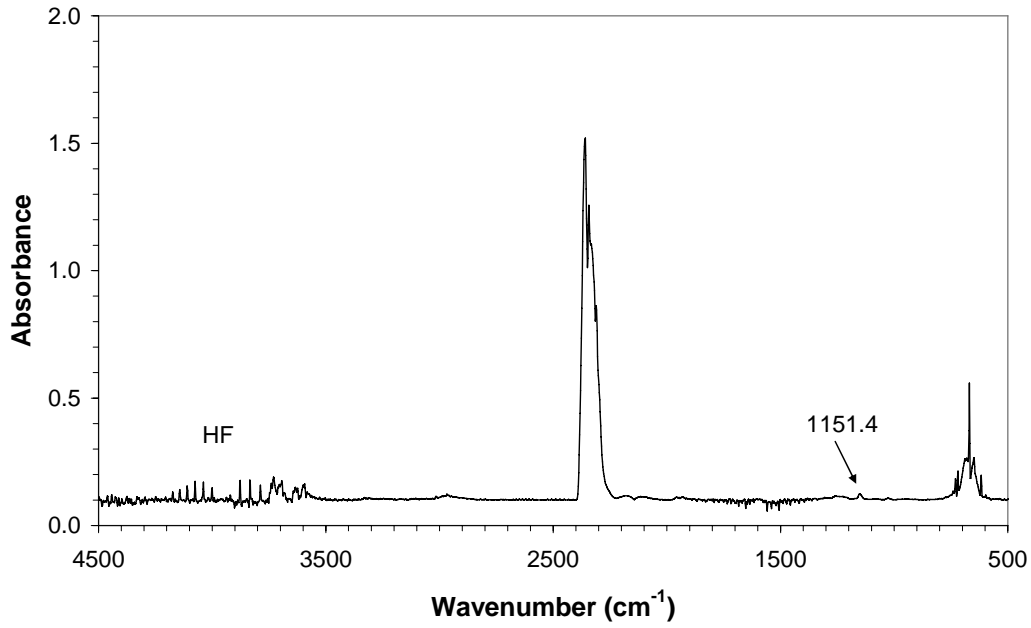


Figure C 23. FTIR spectrum from test with 56 % Halon 1301.

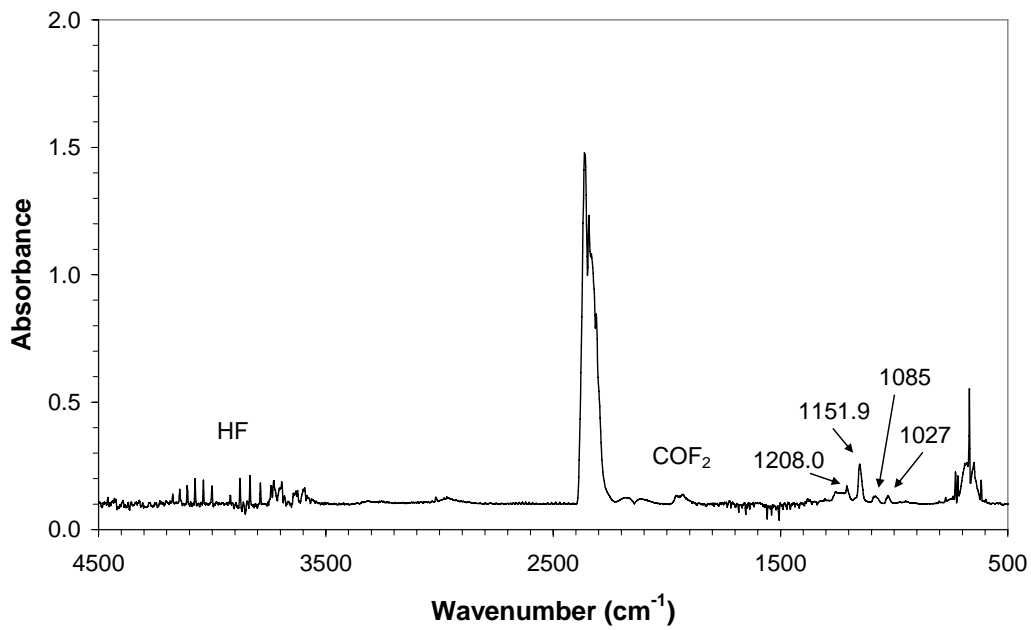


Figure C 24. FTIR spectrum from test with 86 % Halon 1301.

Table C 9. Results from analysis of fluorine content of FTIR filter.

Extinction agent	Number of tests sampled with one filter	Total F content in filter from analysis (mg)	Calculated loss of HF in filter (mg)	Total HF trough FTIR gas cell (mg)	Loss of HF in filter (%)
HFC 227	7 tests	9.2	9.69	191	4.8
HFC 227	1 × 10 min	0.37	0.39	17.4	2.2
HFC 227	1 × 20 min	0.35	0.37	36.3	1.0
HFC 125	6 tests	6.6	6.95	115	5.7
Halon 1301	3 tests	0.28	0.29	10.6	2.7
“C ₆ F ₁₂ -ketone”	3 tests	1.6	1.68	66.8	2.5

Table C 10. Results from analysis of bromine content of FTIR filter.

Extinction agent	Number of tests sampled with one filter	Total Br content in filter from analysis (mg)	Calculated loss of HBr in filter (mg)	Total HBr trough FTIR gas cell (mg)	Loss of HBr in filter (%)
Halon 1301	3 tests	0.081	0.082	12.0	0.68