ANALYSIS AND IDENTIFICATION OF THE BREAKDOWN PRODUCTS OF POTENTIAL EXTINGUISHING AGENTS SUBJECTED TO FLAMING COMBUSTION.

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ABSTRACT

QinetiQ has performed some preliminary, qualitative studies to identify the types of species produced when potential halon replacement agents are passed through a flaming combustion zone. Initial analysis was performed using an FTIR (Fourier Transform Infra Red), which allowed identification of some structural components/functional groups present in the compounds. Further analysis to more fully identify the compounds produced was performed by using a GC/MS (gas chromatography with mass spectrometry), which facilitated modification of the injection and method conditions to optimise the analysis across the wide chemical range of compounds investigated.

BACKGROUND

One element of significant concern when developing novel fire extinguishing agents is the toxicity of the compounds. If compounds are found to have significant mammalian toxicity, this will reduce the scope of applications in which the agent can be employed, for example the uses would be restricted to unoccupied spaces. This will affect the viability of the compound as a potential halon replacement agent.

However, relatively little attention is focussed on the breakdown products of the potential agents which may be formed during exposure of the agent to flaming combustion during deployment. Toxicity of the breakdown products may be a significant factor in some applications, for example in operational defence situations where personnel cannot leave the affected area. Also, the production of compounds that are corrosive in nature may preclude them from use in facilities, or on equipment which is sensitive to such compounds, for example, electronic equipment in communications and control centres which need to maintain operational effectiveness. This was initially a defence concern, but with increased reliance on computer based control system in the modern environment, this criteria is becoming more widely applicable.

COMBUSTION METHODOLOGY

QinetiQ has performed some preliminary qualitative studies to identify the types of species produced when potential halon replacement agents are passed through a flaming combustion zone. The Meker Burner equipment was employed to provide the combustion model. This consists of a methane/air flame, with the agents mixed into the air flow prior to entering the combustion zone (shown in Figure 1). Indicative thermocouple measurements of the flame temperature showed the hottest flame region to be stable at approximately 900-920^{O}C. A collar of nitrogen gas rises from near the base of the burner, and the burner with the 'nitrogen collar' are isolated from the surrounding environment by a glass chimney. The original chimney design was enclosed, with two ports at the top to pump out sample gases at the desired rate. This design was found to induce premature extinguishing of the burner flame due to the build up of combustion products, and associated back pressure. The current chimney now has an open top, and a glass filter funnel system is positioned directly above the gaseous stream from the combustion zone. The sample required is extracted by pumping through the funnel, complete with filter to remove any particulate, and into the collection system, which varies according to the analysis method subsequently employed. Liquid or gaseous agents can be studied by this method.

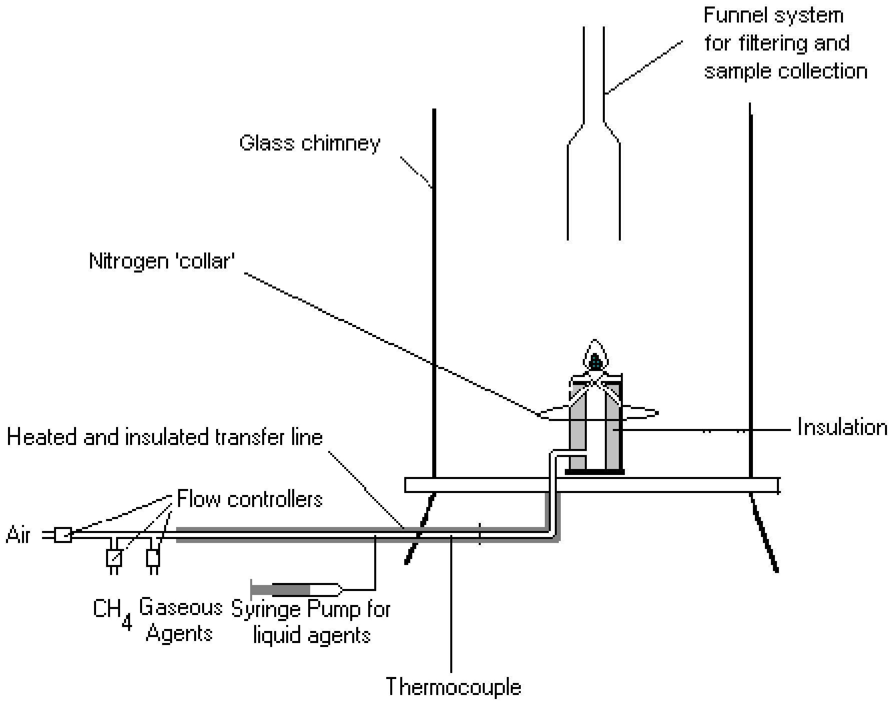

Figure 1. Meker burner equipment.

ANALYSIS METHODOLOGY

For all of the extinguishants used in this study where the Meker burner was employed as the combustion model, the agents were added into the flame at approximately half of their measured extinguishing concentration on the FID. This was to use the agent in an inefficient manner, in order to maximise the potential for toxic and corrosive combustion product formation, and hence consider the worst case scenario.

Infrared

Initial analysis was performed using an FTIR. The combustion effluent was continuously pumped directly from the filter system through a heated line into heated the gas cell of an FTIR. The heated line and cell were maintained at a temperature of approximately $200^{O}C$, and the FTIR was set to scan wave numbers from 4200 to 900, over a time period of 5 minutes, with one scan about every 30 seconds. The pump rate at which the combustion products were drawn through the gas cell was measured at approximately 2.5 litres min^{-1}.

Gas chromatography

In order to further analyse the agent combustion products, following the limited level of compound identification from the FTIR scans, GC/MS was subsequently performed. Due to the logistics and limited mobility of the equipment employed, gaseous samples for GC/MS analysis were collected by means of drawing the combustion effluent into a 5 litre Tedlar gas sampling bag, using a peristaltic pump. The GC was fitted with 30m HP-5MS capillary column with an inner diameter of 0.25mm and an inner coating of 0.25µm stationary phase. The stationary phase consists of 95% dimethylsiloxane and 5% phenylmethyl polysiloxane in a single polymer. The sample gas from the Tedlar bag was introduced into the GC carrier gas via an automated sample valve fitted with a 500µl sample loop. The run methodology used was as follows:

GC conditions		**MS conditions**		
Inlet temp	250°C	Detector threshold	150 eV	
Inlet initial pressure	3.5psi	Tune type	Standard spectra	
Injector split ratio	4.8	0-10 min	Scan range	10 - 250 amu
Column flow	1.6ml min^{-1}		Scan rate	3.06 scans / s
Operating mode	Constant flow	10-20 min	Scan range	20 - 500 amu
Initial oven temp	-20°C		Scan rate	3.06 scans / s
Oven ramp rate	12.5°C min^{-1}	20 min - end	Scan range	20 - 700 amu
Final oven temp	260°C		Scan rate	2.20 scans / s
MS transfer line temp	280°C			
Hold at final temp	4 min			
Total run time	26.4 min			

Pyro-injector

Due to the chemical nature of the compounds being analysed, it was necessary to do direct GC/MS analysis to avoid significant attenuation of the phosphorus containing species in the sample collection system. Using this technique means that the degradation of the agents is largely non-oxidative (a small amount of air would be introduced during sample injection), whereas the agents burnt in the Meker burner are in an oxidative combustion atmosphere. This method directly injected the agents under investigation into the pyro-injector inlet (an SGE Pyroinjector II pyrolysis unit), on the GC. The pyro-injector was set to a temperature to simulate that measured in the Meker burner flame, $900^{O}C$. The volume of sample injected was 2µl, the initial pressure was 2.6psi, and the septum purge was set to off. The full run methodology was:

GC conditions

Inlet temp	250°C
Inlet initial pressure	1.1psi
Injector split ratio	4.8
Column flow	1.2ml min^{-1}
Operating mode	Constant flow
Initial oven temp	-60°C
Oven ramp rate	6°C min^{-1}
Final oven temp	260°C
MS transfer line temp	280°C
Hold at final temp	7 min
Total run time	60.33 min

MS conditions

Detector threshold	150 eV
Tune type	Standard spectra
Scan range	20 - 700 amu
Scan rate	2.20 scans / s

Ion chromatography

IC was performed in order to capture and identify, in a semi-quantitative manner, any halide gases generated during the combustion of the agents tested. The combustion and sample collection methodology was as described for gas chromatography, with the exception that a bottle containing 100ml of 0.1M NaOH was substituted for the gas sample bag, and the combustion effluent was bubbled through the collecting liquid at a rate of 160mlmin^{-1}. The length of time for which sample was collected was recorded for each sample. A 25µl aliquot from each 100ml sample was run through the IC, and quantitative values for chloride, bromide and fluoride ions were calculated with reference to calibrated standards. The calculation involved reference to the total amount of combustion effluent bubbled through the liquid collection media, and included a conversion from the liquid back to the gas phase. The results can only be considered to be semi-quantitative due to the Meker burner set-up, where the open chimney system means that capture of the entire combustion effluent cannot be guaranteed.

RESULTS

Infrared

The results from the FTIR analysis did not identify any specific combustion products generated by agent degradation, despite comparison with extensive electronic chemical compound libraries. The peaks were manually identified, and this information allowed identification of some areas of the chemical structures and functional groups contained in the compounds. These structural components are listed in Table 1.

Compound	Components detected
Halon 1011 [Bromochloromethane]	dihalogen compounds, -C=O, -C-F
Compound # 873 [2-bromo-3,3,3-trifluoropropene]	-C=C-, -C=O, -C-F, dihalogen compounds, acid halides
Compound # 903 [4-bromo-3,3,4,4-tetrafluorobutene]	-C=O, -C-F, dihalogen compounds, acid halides
Compound # 1116 [2-bromo-3,3,4,4,4-pentafluorobutene]	-C=C-, -C=O, -C-F, dihalogen compounds, acid halides
Bis (2,2,2-trifluoroethyl) 2,2,3,3,3-pentafluoropropyl phosphate	-P-H, -P-O-H, -P-C-, -P=O
Tris (2,2,2-trifluoroethyl) phosphate	CH_4, -C=N, -N-H, -P-C-, -P=O
Tris (2,2,3,3,3-pentafluoro-1-propyl) phosphate	CH_4, -C=N, -N-H, -P-C-, -P=O
Tris (2,2,3,3,4,4,4-heptafluoro-1-butyl) phosphate	CH_4, -C=N, -N-H, -P-H, -P-C-, -P=O

Table 1. Structural components identified by FTIR with manual analysis

Gas chromatography and pyro-injector

The GC/MS work on the combustion effluent samples collected in the Tedlar gas bags identified a number of compounds originating from the halogenated hydrocarbon agents. All samples showed some unaltered agent. There were also compounds that were reaction products, believed to be derived from the fluorine containing breakdown products reacting with the GC column lining, these are the silanes. The phosphorus containing compounds did not show significant peaks when run on the GC/MS. It is believed that their degradation products may, like the original agents, have high boiling points, so might be condensing out in the sampling system or gas bag (although this could not be visually confirmed).

The problems with collecting and transferring the degradation products from the phosphorus containing agents lead to the use of the pyro-injector technique with the GC/MS to ensure that the compounds reached the GC column and mass spectrometer. This method was successful in separating the compound peaks of the phosphorus containing degradation products, but the electronic libraries were unable to determine the identities of many of the species. Therefore identification of the compounds was performed manually. The results from both the standard GC/MS analysis, and the pyro-injector GC/MS are presented in Table 2. Any silane compounds are again derived from the reaction of the agent breakdown products with the GC column.

Compound	**Standard GC/MS**	**Pyro-injector GC/MS**
Halon 1011 [Bromochloromethane]	Bromochloromethane; Methylenechloride; and Ethanol	Hydrochloric acid; Hydrobromic acid; Bromomethane; Bromoethene; Chlorobenzodioxole; Benzene; Dibromoethane; Chlorobenzene; Bromobenzene; Hexamethylcyclotrisiloxane; Dichlorobenzene; Methyloxyphenol; Acetophenone; Bromochlorobenzene; Decamethylcyclopentasiloxane; Bromoethenylbenzene; Trichlorobenzene; Dibromobenzene; Bromodichlorobenzene; Dibromochlorobenzene; Triphenylindole; Chloronaphthalene; Tribromobenzene; Bromonaphthalene; Dichloronaphthalene; Bromodichloronaphthalene; Dibromonaphthalene; Anthracene; Chloroanthracene; Bromophenanthrene; $C_5H_3Cl_3N_2Si$; and a range of silanes & siloxanes
Compound # 873 [2-bromo-3,3,3-trifluoropropene]	2-Bromo-3,3,3-trifluoropropene; Fluoromethane; and Fluoromethanol	Trifluorosilane; Hydrochloric acid; Hydrobromic acid; Bromomethane; Bromodifluoroethene; Dibromomethane; Bromofluorobenzene; $CF_3CF_2CF_2OF$; Trifluorobenzene; Tetrafluorobenzene; Trifluoromethyltetrafluorobenzene; Dodecafluorocyclohexane; Trifluoromethyltrifluorobenzene; Pentafluorobromomethylbenzene; Decafluoropentene; Heptafluoroxylene; Trifluorotrifluoromethylbenzene; Tris(trifluoromethyl)fluorobenzene; Trifluoromethylbenzene; Difluorotrifluoromethylbenzene; Octafluorotrifluoromethylcyclopentane; Bromoheptafluoroxylene; Bis(trifluoromethyl)benzene; Bis(trifluoromethyl)bromobenzene; Fluoromethylbromo tetrafluorobenzene; Pentafluoroethenylbromotetrafluoro benzene; Tribromobenzene; Bromotetrafluorobenzene; Tribromofluorobenzene; Bromodifluorobenzene; Dibromotrifluorobenzene; Bis(trifluoromethyl)bromodifluoro benzene; Difluoromethylbromodifluorobenzene; Difluoromethyldibromotrifluorobenzene; Trifluoromethyldibromofluorobenzene; $C_8HBrF_6OSF_4$; Tribromotrifluorobenzene;

Compound	**Standard GC/MS**	**Pyro-injector GC/MS**
		Dibromotetrafluorobenzene; and Dibromomethylacridione
Compound # 903 [4-bromo-3,3,4,4-tetrafluorobutene]	4-Bromo-3,3,4,4-tetrafluorobutene; Bromotrifluoropropene; Trifluoroethanol; Fluoromethylsilane; Fluorotrimethylsilane; Difluorosilane; and Ethanol	No compound available for testing
Compound # 1116 [2-bromo-3,3,4,4,4-pentafluorobutene]	2-Bromo-3,3,4,4,4-pentafluorobutene; Bromotrifluoroacetone; Trifluoroethanol; Bromotrifluoropropene; Fluoromethylsilane; and Ethanol	Pentafluoroethane; Hydrobromic acid; Bromodifluoromethane; Bromodifluoroethene; Trifluorobenzene; Pentafluorobenzene; Heptafluorobenzene; Tetrafluorobenzene; Bis(trifluoromethyl)tetrafluorobenzene; Bis(trifluoromethyl)difluoromethyl trifluorobenzene; Difluoromethyltetrafluorobenzene; Pentafluoroethyltetrafluorobenzene; Tetrafluoroethyltetrafluorobenzene; Trifluoromethyltetrafluorobenzene; Trifluoromethyltetrafluorobenzene; Bis(trifluoromethyl)pyrimidole; Tris(trifluoromethyl)difluorobenzene; Bis(trifluoromethyl)difluorobenzene; Heptafluoroxylene; Difluorotrifluoromethylbenzene; Difluoromethylpentafluorobenzene; Trifluoromethylfluoromethyltetrafluorobenzene; Bromotrifluoromethylpyrimidinamine; Bromofluoromethyltetrafluorobenzene; Bromodifluoroethylbenzene; Bromotrifluoroethyltetrafluorobenzene; Bromotetrafluoromethylbenzene; Dibromomethylpentafluorobenzene; Bromotetrafluoroethyltetrafluorobenzene; Bromotrifluoroethyltetrafluorobenzene; Bromodifluoromethyltetrafluorobenzene; Bromotrifluoroethyltetrafluorocyclo hexadiene; Dibromobis(trifluoromethyl)methylbenzene; Dibromodifluoroethyltrifluorobenzene; Dibromofluoromethyltrifluorobenzene; Dibromodifluoromethyltrifluorobenzene; Dibromotrifluoromethyltrifluorobenzene; Tribromotrifluoromethyldifluorobenzene; Tribromodifluoromethyldifluorobenzene

Compound	Standard GC/MS	Pyro-injector GC/MS
Bis(2,2,2-trifluoroethyl) 2,2,3,3,3-pentafluoropropyl phosphate		Trifluoromethanol; Pentafluoroethane; Pentafluoropropane; Trifluoropropene; Trifluoropropane; Tetrafluorosilane; Bis(methyl)silylphosphate; Difluorobenzene; Fluorobenzene; Trifluorobenzene; Bis(pentafluoropropyl)fluorophosphate; Bis(pentafluoropropyl)phosphate; and a range of silanes & siloxanes
Tris(2,2,2-trifluoroethyl) phosphate		Pentafluorobutene; Tetrafluorosilane; Trifluoroethanol; Trifluorobenzene; Difluorotrifluoromethylbenzene; Benzene; Difluorobenzene; Fluorobenzene; Difluoromethylbenzene; Difluoromethyldifluorobenzene; Trifluoromethylbenzene; Fluorotrifluoromethylbenzene; Tris(trifluoroethyl)phosphate; Difluoroethenylfluorobenzene; F_3CCH_2OF; H_2PCF_3; $HCPF(CF_3)$; $H_2PO(OC_2H_5)$; and $(CH_3)_2PFO$
Tris(2,2,3,3,3-pentafluoro-1-propyl) phosphate		Tetrafluorosilane; Dimethylfluoro phosphate Difluoroethyoxytrifluoromethylmethylphosphine; Pentafluoropropanol; Fluoroethoxysiloxyphosphite; Ethynediyltrimethylsilanebimethylsilane; Benzene; Fluorobenzene; Methylpentafluorobenzylphosphorous oxide; Bis(pentafluoropropyl)trifluoromethylphosphate; Pentafluoropropyltrifluoromethylmethyl phosphate; Heptafluoropropylpentafluoropropylfluoro methyl phosphate; Bis(fluoromethyl)silylphosphate; Fluoromethylfluorosilylmethylphosphate; Haxamethylcyclotrisiloxane; $P_2O_5C_{11}H_9F_{19}$; Octamethylcyclotetrasiloxane; $POC_3H_{13}Si_2$; Fluorooctamethylcyclotetrasiloxane; and a range of silanes & siloxanes

Compound	Standard GC/MS	Pyro-injector GC/MS
Tris(2,2,3,3,4,4,4-heptafluoro-1-butyl) phosphate		Tris(heptafluorobutyl)phosphate; Difluorodimethylsilane; Tetrafluorosilane; Heptafluorobutanol; Phosphoric acid; Decamethylcyclopentasiloxane; Benzene; Fluorobenzene; Fluorohydroxymethyl trifluoromethylphosphine; Hexamethylcyclotrisiloxane; Ethynylfluoromethyltrifluoromethylsilyl phosphate; Bis(pentafluorobenzyl)heptafluorobutyl phosphate; Bis(heptafluorobutyl)heptafluorosilylbutyl phosphate; Trimethylsilylbimethyltrifluorosilylfluoro hydroethenylphosphate; $C_{10}F_{11}H_5Osi$; and a range of silanes & siloxanes

Table 2. Compounds identified by standard GC/MS and GC/MS with pyro-injector

Ion chromatography

Supplementary tests were run on selected agents in order to determine the levels of halide compounds generated under inefficient extinguishing conditions. Although concentration (ppm) values are presented in Table 3, these should only be considered in a comparative manner between the compounds listed.

Compound	F^- (ppm)	Br^- (ppm)	Cl^- (ppm)
Halon 1011 [bromochloromethane]	N/A	12	21
Compound # 873 [2-bromo-3,3,3-trifluoropropene]	151	7	N/A
Compound # 1116 [2-bromo-3,3,4,4,4-pentafluorobutene]	63	2	N/A

Table 3. Semi-quantitative results for halide content of agent combustion effluent

DISCUSSION AND CONCLUSIONS

The results from the FTIR analysis were useful in that they provided initial indications of the type of functional groups that were produced when the agents were subjected to oxidative combustion and inefficient extinguishing conditions.

The standard GC/MS analysis indicated that the halogenated hydrocarbon agents under oxidative combustion and inefficient extinguishing conditions generated a few detectable breakdown products. The analysis also showed the presence of some unreacted agent, and some silane compounds, which are thought to be reaction products of fluorine containing breakdown products with the GC column. This methodology was unsuccessful on the phosphorus containing compounds, and minimal peaks were observed. It is believed that any breakdown products formed had sufficiently high boiling points to become trapped in the sampling system, so did not reach the GC column to be separated and identified.

The GC/MS with the pyro-injector appeared to overcome this problem, by directly injecting the agent into the high temperature ($900^{O}C$) unit. This meant that any thermal breakdown of the agent would occur at a similar temperature to that measured in the Meker burner flame. However, the environment would be predominantly non-oxidative (with the exception of a small quantity of air injected with the sample), in contrast to the Meker burner flame. A large number of compounds were detected by this method, as can be seen in Table 2. Some of these are derived from breakdown product reactions with the GC column to form silane and siloxane compounds. A significant number of the compounds detected have aromatic character. This may be due to the non-oxidative conditions in the thermal decomposition environment.

This work was performed with a view to determining whether, in a worst case extinguishing scenario, the agents under test would produce significant numbers and quantities of compounds that may be toxic to humans and/or corrosive to equipment. This study has successfully identified many compounds that may be produced. Some compounds, such as the acids, are corrosive by nature, and may cause problems if produced in sufficient quantities. Benzene, and some of the other aromatics that are more commonly encountered in industrial environments, are known to induce mutagenic and carcinogenic effects. However, the toxicity of many of the compounds is not readily known, and work in this area is ongoing.

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