SCREENING AND CHARACTERIZATION OF SECOND-GENERATION HALON REPLACEMENTS

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ABSTRACT

This paper describes an innovative method for the screening and characterization of second-generation halon replacements. The approach involves the use of computational chemistry techniques to develop quantitative structure-property relations (QSPRs) for key halon properties. QSPRs were developed for cup-burner flame-extinguishing concentration, ozone-depletion potential (ODP), global warming potential (GWP), the reaction rate constant with OH radicals, normal boiling point, inhalation toxicity (4-hour LC_{50}), and cardiac sensitization (no observed adverse effect level). Correlation coefficients (R^2) for the QSPRs ranged from 0.81 to 0.96. These QSPRs were then used to predict the unmeasured properties for a database containing approximately 350 halogenated organic compounds with 1-4 carbon atoms. The results of the QSPR predictions were used to select a short list of previously untested candidate replacement agents for experimental evaluation. The selection procedure first eliminated any compound with a literature or calculated ODP above 0.2. The compounds were then subdivided into either streaming or flooding candidates based on their boiling point. Compounds with flame-extinguishing concentrations of greater than 6% were then eliminated. Streaming and flooding agent candidates with no previous flame-extinguishing data were then selected based on cost, availability, toxicity, GWP, and OH radical reaction rate constant. **A** total of seven streaming agent candidates and three flooding agent candidates (all previously untested) were selected for experimental characterization. Experimental measurements currently being made on these agents include flame-extinguishing concentration (cup burner), vapor pressure/temperature, and materials compatibility. Candidates showing a high probability for success will be subjected to toxicity testing.

INTRODUCTION

The goal of this project was to develop a screening technique for second-generation halon replacements that would allow consideration of halocarbon-type compounds with unmeasured properties. While many compounds have been experimentally investigated as potential replacements, many more compounds exist that have not been experimentally characterized. Our approach was to apply the techniques of computational chemistry to develop quantitative structure-property relations (QSPRs) that correlated structural features of molecules (molecular connectivity, atom and bond types and counts, etc.) to key halon replacement properties. Once developed, the QSPRs were used to predict the key properties of a large set of potential replacements with previously unmeasured properties. Compounds with promising properties were then selected for experimental evaluation.

The computational chemistry system used to develop QSPRs was ADAPT, developed by Dr. Peter Jurs at Penn State University. The general procedure used to develop QSPRs was:

1. Select a data set of compounds and their properties of interest.
2. Draw the molecular structures with molecular drawing software and enter the structures into ADAPT.
3. Generate computational-chemistry-based molecular descriptors for the compounds in the study set. ADAPT can generate approximately 150 descriptors that are based on topological, geometrical, electronic, or physicochemical features of the molecule.
4. Identify redundant descriptors using statistical techniques. This step creates a set of unique descriptors.
5. Develop QSPRs using multiple regression or other statistical techniques that correlate the property of interest to the molecular descriptors.
6. Investigate the QSPRs for internal consistency and statistical significance, and select the best QSPR for each property of interest.
7. Draw the molecular structures of the compounds that will have their property predicted by the QSPR, and generate the necessary descriptors for those compounds.
8. Use the QSPR to predict the property of the compounds of interest.

DATA COLLECTION AND QSPR DEVELOPMENT

We developed QSPRs that would allow for screening of flame-extinguishing effectiveness, toxicity, agent volatility, and atmospheric impact. The flame extinguishing concentration (FEC) as measured by the cup burner apparatus was selected as a measure of flame-extinguishing effectiveness. Cardiac sensitization (NOAEL) and inhalation toxicity (4-hour rat and mouse LC_{50}) were selected as measures of toxicity. The normal boiling point was selected as a measure of agent volatility, and ODP, GWP, and OH-radical reaction rate constant (which is used to calculate tropospheric lifetime) were used as measures of atmospheric impact. A database of approximately 350 halocarbon-type compounds was compiled for the QSPR development.

Two QSPR sets were developed for each property. The original QSPRs were developed early in the project using data available in the open technical literature[1-8] and commercial databases[9-10]. Updated QSPRs were developed later in the project that incorporated updated data or new property measurements[11-15] (including measurements made on this project). Table 1 lists the number of compounds from specific halocarbon families used to develop the updated QSPRs. The QSPRs developed were multi-dimensional linear equations that used ADAPT descriptors as independent variables and the property of interest as the dependent variable. Table 2 lists the QSPRs and their statistical parameters. The QSPRs were then used to predict the unmeasured properties of the compounds in the database.

Table 1 - Population of Halocarbon Families Used For QSPR Development							
Family	**FEC**	**Boiling Point**	**k OH**	**GWP**	**ODP**	**Cardiac Sensit.**	**LC_{50}**
Chlorocarbons	1	2	0	1	1	*0*	1
Hydrochlorocarbons	6	26	13	1	2	2	6
Fluorocarbons	11	14	0	2	0	5	2
Hydrofluorocarbons	11	17	14	12	0	6	5
Fluorinated Ethers	8	11	4	0	0	0	0
Halogenated Ethers	0	11	4	0	0	0	2
Chlorofluorocarbons	7	12	0	6	7	5	1
Hydrochlorofluorocarbons	9	21	32	7	10	4	6
Bromofluorocarbons	5	12	0	1	2	1	0
Hydrobromofluorocarbons	8	20	8	0	2	0	0
Bromochlorofluorocarbons	1	4	0	0	1	1	1
Hydrobromochlorofluorocarbons	3	7	2	0	1	0	0
Hydrobromocarbons	1	*9*	14	0	1	0	3
Hydrobromochlorocarbons	1	3	6	0	0	0	0
Bromochlorocarbons	0	0	0	0	0	0	0
Fluoroiodocarbons	4	10	0	1	0	3	5
Hydroiodocarbons	0	6	1	0	0	0	3
Hydroiodofluorocarbons	1	7	0	0	0	0	2
Alkenes	5	40	11	0	0	2	11
Others	0	6	8	0	0	3	0
Totals	***82***	***248***	***117***	***31***	***27***	***32***	***48***

Table 2 - QSPRs For Key Properties

$$\log_{10} FEC = 1.0905 - 1.06662*NBPH + 0.267168*NCPH - 0.038542*MPOL$$

$R^2 = 0.82670$ F-statistic = 124

$$T_{boil}(K) = 126.50 + 8.03475*MREF - 68.8703*S4C + 3.05885*KAPA3 - 182.63*QNEG - 21.4152*NI - 15.1988*NDB$$

$R^2 = 0.95820$ F-statistic = 921

$$\log_{10} kOH = -13.0879 - 2.56073*NFPH + 1.37112*NDB - 0.272546*KAPA5$$

$R^2 = 0.90288$ F-statistic = 350

$$\log_{10} GWP = 1.56553 + LALT + 0.825186*SYMM$$

$R^2 = 0.88867$ F-statistic = 112

$$\log_{10} ODP = -1.87774 + 6.98571*NBPH + 2.91096*NCPH + 0.348265*S6C + 2.16010*NFPH - 0.797889*KAPA2$$

$R^2 = 0.90047$ F-statistic = 38

$$\log_{10} NOAEL = -2.67942 + 770.883/TB + 0.50084*KAPA2 - 1.17266*NI - 0.92743*SYMM - 4.26405*V6C$$

$R^2 = 0.94374$ F-statistic = 87

$$\log_{10} LC_{50} = 4.02862 - 1.60269*NDB - 1.73734*V1 + 0.99212*V2 - 1.39834*V3C - 6.08127*V6C + 1.15593*V5PC + 2.04658*S4C + 8.72762*QNEG$$

$R^2 = 0.82670$ F-statistic = 124

Descriptor Definitions

NFPH = number of fluorine atoms/potential halogen sites
NCPH = number of chlorine atoms/potential halogen sites
NBPH = number of bromine atoms/potential halogen sites
NI = number of iodine atoms
NDB = number of double bonds
LALT = log atmospheric lifetime (yrs.)
TB = normal boilingpoint (K)
QNEG = charge on most negative atom of molecule
SYMM = structural symmetry descriptor
MPOL = molecular polarizability descriptor
MREF = molar refraction descriptor
V1, V2, V3C, V5PC, V6C, S4C, ***S6C*** *= molecular connectivity descriptors*
KAPA2, KAPA3, ***KAPA5*** *= kappa indices*

CANDIDATE REPLACEMENT COMPOUND SELECTION

We developed a selection criteria in order to identify those compounds that showed potential as halon replacements. If experimental data for a specific property of a compound was available, it was used in the database. If experimental data was unavailable, the value of the property predicted by the original QSPR was used. The selection procedure is described below.

1. Eliminate any compound with either a predicted or literature value of ODP greater than 0.2. This cutoff was enforced to comply with EPA requirements.

2. Divide the surviving group of compounds into flooding agents (normal boiling point between -80°C and -10°C) and streaming agents (normal boiling point between -10°C and 90°C).

3. Rank each of the agents from lowest to highest value of FEC. **A** cut-off of a FEC of 6 was established, using an FEC of 5 or less (a feasible/nonfeasible threshold) plus-or-minus the absolute error of the QSPR, which was 1.00.

4. Select compounds based on minimizing FEC, atmospheric lifetime, ODP, GWP, toxicity characteristics, compound availability, and whether or not the compound had been previously investigated as a halon replacement.

Table 3 lists the ten candidate replacement agents that were selected based on the above criteria. Two agent standards were also selected for evaluation; perfluoro-n-hexane and octafluoropropane. These materials have flame-extinguishing concentration values previously reported in literature, and consequently, these values served as a comparison to those measured with Mainstream's cup-burner apparatus.

Table 3 - Candidate Agents Selected For Experimental Evaluation

	Tboil (°C)	FEC (%)	ODP
Streaming Agents			
HBFC-12	110	1.8	0.12
HIFC-02	49	2.7	0.00
ALK-65	30 *	2.7	0.00
KET-23	86 *	3.2	0.02
PFE-13	107	3.6	0.00
PFE-14	11	6.3	0.00
HBFC-17	25	3.7	0.18
Flooding Agents			
ALK-06	-29 *	**7.4**	0.00
PFC-02	-21	6.6	0.00
ALK-46	-3 *	6.6	0.00

* indicates experimental data; all other values are ADAPT predictions

EXPERIMENTAL EVALUATION

Experimental evaluation of the selected agents consisted of measuring their cup burner concentration in a cup burner apparatus, determining their vapor pressure/temperature characteristics, determining materials compatibility with various metals and non-metals, and measuring their residue level. Selected agents were also subjected to inhalation toxicity testing.

Flame-Extinguishing Concentration

We developed a cup burner apparatus 41 cm in height with an OD of 5 cm, constructed of standard thickness (1.5 mm) glass tubing. Ground glass side ports were installed for temperature measurement and flame ignition. Glass beads were placed at the agent/air inlet to the system to facilitate mixing. The system provides for independent adjustment and measurement of the air and agent flow rates and pressures. The air enters at the bottom of the mixing section where it is mixed with the agent. Liquid agents (i.e., boiling points above room temperature) are pumped via peristaltic pump to the mixing chamber, passing through a preheated plenum to vaporize the agent. The mixing section is immersed in a constant temperature water bath, held at a temperature 30°C above the boiling point of the agent. After the air and agent streams are mixed, they pass upward through finger baffles and then glass beads to induce further mixing. The stream then enters the chimney section where it contacts the n-heptane fuel flame. The level of the n-heptane fuel in the cup is controlled by a peristaltic pump. The results of the measurements are given in Table 4.

Table 4 - FEC Measurements

	Measured FEC	Predicted or Literature FEC	Reynolds Number (cup)
Streaming Agents			
perfluorohexane (standard)	4.0%	4.4% (Literature)	219
HBFC-12	2.7%	1.8%	358
PFE-13	3.5%	3.6%	211
HIFC-02	3.7%	2.7%	246
HBFC-17	3.7%	3.7%	260
KET-23	4.4%	3.2%	287
ALK-65	4.6%	2.7%	338
PFE-14	11.7%	6.3%	308
Flooding Agents			
octafluoropropane (standard)	5.6%	6.1% (Literature)	306
PFC-02	4.2%	6.3%	461
ALK-46	4.9%	6.6%	477
ALK-06	4.9%	6.6%	385

Vapor Pressure/Temperature Characteristics

Two techniques were used for measuring saturated vapor pressure/temperature characteristics; a high-pressure differential scanning calorimeter (DSC) technique and a classical liquidvapor equilibria technique. These techniques are described elsewhere[12, 16-17]. The normal boiling points of the agents can also be determined from these measurements. The DSC technique is typically used for samples with normal boiling points above 40°C while the liquidvapor equilibria technique is typically used for samples with normal boiling points below 40°C. Table 5 presents the measured boiling points of the agents and compares these results with the ADAPT predictions. The average error in the ADAPT boiling point predictions was 4.09%. The table shows that there are three possible flooding agents. All other agents would have to be considered streaming agents because of their higher boiling points.

Table 5 - Normal Boiling Points For Candidate Agents and Agent Standards

	Method	Tboil ("C)	Predicted Tboil (°C)
Streaming Agents			
perfluoro-n-hexane (standard)	DSC	57.37	n/a
PFE-14	classical	28.25	10.85
ALK-65	classical	31.47	63.90
HBFC-17	classical	35.11	24.50
HIFC-02	DSC	56.55	48.60
KET-23	DSC	90.3	86.0
PFE-13	DSC	104.76	106.60
HBFC-12	DSC	116.88	110.10
Flooding Agents			
octafluoropropane (standard)	classical	-37.76	n/a
ALK-06	classical	-30.08	-19.40
PFC-02	classical	-0.56	-20.70
ALK-46	classical	0.75	3.50

Materials Compatibility

A test method to determine the materials compatibility of various materials exposed to the candidate agents has been developed. The method is a modification of NIST test methods[15, 18]. The method involves supporting the various metal and nonmetal samples in a container filled with the candidate agent in the liquid phase. The apparatus consisted a thick-walled glass pressure tube that has a glass thread at the top and a threaded plunger valve that allowed for evacuation of the tube and charging with an agent. The tube was 17.8 cm in length with an OD of 25.4 mm. The metals and nonmetals tested were Nitronic 40, copper CDA 172, aluminum 6061-T6, 1020 alloy steel, Teflon TFE, silicon rubber, Buna-N, and Viton. Circular coupons of these materials that measured 1/2" OD, 1/16" thick, with a 9/64" OD hole in the center were used. A Teflon rod passed through the hole and suspended the coupon, small Teflon spacers separated the coupons from one another. Two coupons from each material were used for each test. The test time was 29 days and the test temperature was room temperature. The samples were precleaned prior to the test ultrasonically in acetone, weighed on an analytical balance, and their dimensions are measured. After the test, the samples are cleaned, weighed, and measured again. The materials were then examined under a microscope for any change in appearance. Table 6 presents the materials compatibility results for the metal samples tested. The corrosion rates are listed are average values for the two metal samples of each material. The values with a "less-than" ("<") correspond to a mass change less than the sensitivity of our balance (± 0.1 mg).

Table 6 - Corrosion Rates (mm/year x10^4)

	1020 Steel	Al 6061-T6	Cu CDA 172	Nitronic 40
treaming Agents				
per-uorohexane (standard)	< 1.85	< 10.6	63.4	< 3.58
HBFC-17	37.2	137	446	82.3
HIFC-02	< 1.85	< 10.6	102	28.6
HBFC-12	39.1	21.1	77.6	< 3.58
KET-23	< 1.85	90.6	170	< 3.58
PFE-14	169	21.1	81.1	3.58
ALK-65	263	10.6	481	7.17
PFE-13	1.85	< 10.6	63.4	< 3.58
looding Agents				
octafluoropropane (standard)	9.37	< 10.6	41.4	10.8
ALK-46	48.4	106	184	96.9
PFC-02	< 1.85	21.3	121	10.9
ALK-06	< 1.85	53.2	54.0	7.21

Table 7 presents the results of the materials compatibility tests for the nonmetal samples tested. A compatibility rating was defined based on the percentage change in the thickness of the sample before and after the test. Mass changes and diameter changes of the sample were also measured during the test, and were found to correlate highly with the change in sample thickness. Percent mass changes correlated to percent thickness changes by an average factor of 6.1 (R^2=0.96), percent diametric changes correlated to percent thickness changes by an average factor of 0.57 (R^2=0.92).

Table 7 - Materials Compatibility Results For Nonmetals				
	Buna-N	**Silicon Rubber**	**Viton**	**Teflon**
Streaming Candidates				
perjluorohexane (standard)	B	C	A	B
HBFC-17	D	D	D	B
HIFC-02	D	D	D	B
HBFC-12	D	D	C	C
KET-23	D	C	D	A
PFE-14	B	C	D	A
ALK-65	D	D	C	C
PFE-13	A	C	A	B
Flooding Candidates				
octajluoropropane (standard)	A	B	B	A
ALK-46	B	C	B	A
PFC-02	B	C	B	A
ALK-06	A	C	B	B

A: negligible effect (0-2% thickness change)
B: minor effect (2-5% thickness change)
C: moderate effect (5-15% thickness change)
D: severe effect (>15% thickness change and/or breakage)

Agent Residue Test

The residue level of the candidate agents has been experimentally determined using a method recommended by NIST[18] for screening purposes. If the percent residue level is zero, the agent is listed as Class I. If the percent residue is greater than zero but less than 1, the agent is listed as Class 11. If the percent residue level is greater than 1, the agent is listed as Class III and is unacceptable. The results of this test are provided in Table 8. As this table shows, all of the agents were either class I (zero residue) or class II (less than 1.0%), both of which are acceptable.

Table 8 - Results of Residue Level Experiments		
	% Residue	**Class**
Streaming Candidates		
perfluorohexane (standard)	0.00	I
KET-23	0.04	II
HBFC-12	0.01	II
PFE-13	0.00	I
HIFC-02	0.14	II
ALK-65	0.10	II
HBFC-17	0.02	II
PFE-14	0.02	II
Flooding Candidates		
octafluoropropane (standard)	0.00	I
ALK-46	0.04	II
PFC-02	0.01	II
ALK-06	0.00	I

CURRENT WORK

Current work on this project is focusing on the experimental evaluation of four additional previously-untested candidate agents that were selected based on the updated QSPRs. All of these additional candidates are streaming agents; no additional candidate flooding agents were identified. Experimental evaluations to be performed include FEC measurements, vapor pressure measurements, residue level, and materials compatibility.

We are currently having inhalation toxicity testing performed on several of the most promising candidates. We are testing several of the agents at a test time of 15 minutes (with 10 rats) at a concentration of twice the FEC as measured in our cup burner. Agents that are gases are room temperature will be mixed with air in the appropriate concentration prior to entering the test chamber. Agents that are liquids will be passed through a misting apparatus to volatalize the agent in air.

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