CONF-951262--5
SAND96-0772C

VED
[illegible] 22 1996
OSTI

Instrumentation Advances in Emissions Characterization from Propellant/Explosive Combustion

W. Einfeld and D. J. Morrison
Sandia National Laboratories
Albuquerque, NM

S. E. Mullins
Alliant Techsystems Inc.
Rocket Center, WV

Abstract

Results from a chamber study to characterize emissions from combustion of selected pure energetic materials are presented in this paper. The study was carried out as a part of a comprehensive air pathways risk assessment for a propellant and explosive manufacturing facility that engages in open burning methods for manufacturing waste disposal. Materials selected for emissions characterization in this study included both aluminized and non-aluminized composite propellant, a double base propellant and a plastic bonded explosive. Combustion tests in a specialized chamber revealed very low emissions for gaseous products of incomplete combustion such as carbon monoxide and nitrogen oxides. Analysis of gaseous and aerosol emission products for a pre-selected target analyte list that included both volatile and semi-volatile organics revealed either low or non-detectable emissions for the four energetic types tested. Hydrogen chloride was detected as a major emission product from propellants containing ammonium perchlorate. Results from this work reveal that about one-half of the chlorine in the original material is released as hydrogen chloride. Based on earlier work, the balance of the chlorine emissions is expected to be in the form of chlorine gas.

1. Introduction

In this paper we present results from the emissions characterization component of a health risk assessment carried out for propellant and explosive open burning disposal operations at Alliant Technologies' Allegany Ballistics Laboratory, an energetics manufacturing facility in northern West Virginia. At this facility, waste treatment by open burning occurs both with pure propellants and explosives (P/E) as well as with miscellaneous P/E-contaminated cellulosic and plastic waste material. In this paper, we focus on the results of an emissions characterization project for a double base propellant, several classes of composite propellant and an explosive. Emissions profiles for P/E-contaminated wastes will be reported elsewhere. The considerable magnitude of the facility's burning operation is evidenced by waste mass estimates of 38 metric tons of pure energetics and 77 metric tons of P/E-contaminated waste to be treated at the facility in 1995.

In this study we used a specialized testing facility at Sandia National Laboratories known as the Air Emissions Test Chamber to burn representative samples of energetic waste material in order to measure pollutant emission characteristics for a broad spectrum of chemicals likely to be encountered during full-scale burning operations. This experimental approach enables pollutant emission testing under controlled conditions and in a manner that yields pollutant emission factors which can in turn be used in health risk assessments that employ air dispersion models to estimate pollutant concentrations and potential adverse health effects at receptor sites.

2. Test Chamber Description

The SNL Emissions Test Chamber is a large, air-supported, plastic-coated fabric dome inside which detonation or combustion of energetic material can be conducted without resulting damage to the structure. The chamber, shown in Figure 1, is a 15- m diameter hemispherical dome that is supported by a positive differential air pressure, maintained by a continuously operated blower. Emission products from the test were sampled and analyzed by a

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000.

number of instruments positioned both inside the chamber and in an adjacent mobile lab. Circular blade fans were positioned inside the chamber so that its contents can be thoroughly mixed following a test. The chamber, whose internal volume is known, is tightly sealed such that minimal leakage of combustion products out of the chamber occurs. The combination of a mixed and known chamber volume allows the emissions from a test to be directly related to the starting mass of the test material in order to derive pollutant-specific emission factors.

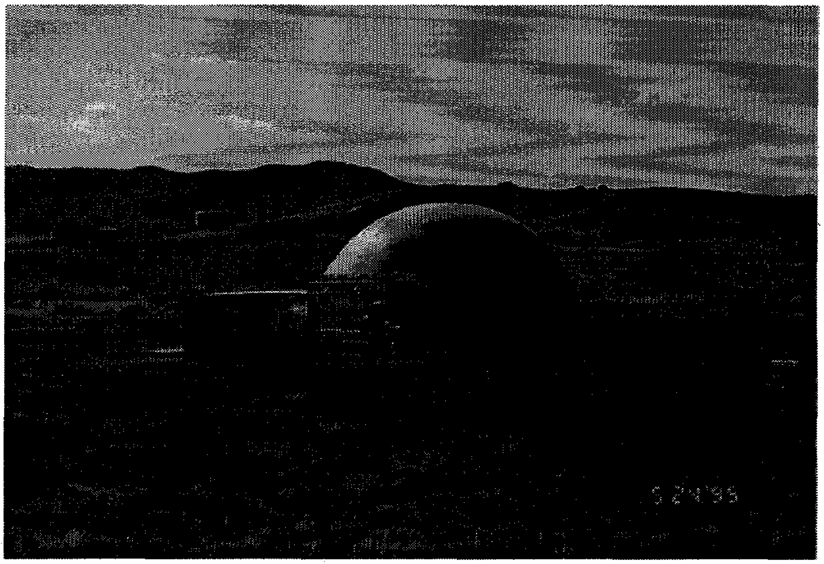

Figure 1 The Air Emissions Test Chamber at Sandia National Laboratories in Albuquerque, New Mexico

A collection of instruments were used in this test series to yield measurements of both gas and aerosol emission products from the various manufacturing waste compositions selected for testing. Table 1 lists the various sampling devices used in the testing program. A photo of the chamber illustrating interior instrument placement is shown in Figure 2.

Table 1 Instrument Systems Used in Chamber Testing

Instrument System	Pollutants Measured
Inside Chamber	
PM-10 Sampler with Quartz Filter	PM-10 Aerosol Concentration.
PS-1 Sampler with Quartz Filter and Resin Cartridge	Semi-Volatile Organic Hydrocarbons
Low Flow Total Filter Sampler with Teflon Filter	Heavy Metal Aerosols
Low Flow Total Filter Sampler with Nylon Filter	Total Nitrate Gas/Aerosol
Low Flow Total Filter Sampler with Mixed Cellulose Ester Filter	Aluminum Aerosol
Low Flow Bubbler System	Total Aerosol Chloride and Ammonia
Open-Path FT-IR Spectrometer	HCl, NH_3 and other reactive gases
Aerodynamic Particle Sizer	Aerosol Size Distribution 0.5-30 micron particle diameter
Outside Chamber	
Continuous Gas Analyzers	CO, NOx, CO_2, SO_2 Gas Concentration
Passivated Stainless Steel Canister	Volatile Organic Hydrocarbons
Closed Cell FT-IR Spectrometer	Reactive gases and other hydrocarbons


5 25 '95

Figure 2 The interior of the test chamber showing several sampling instruments

3. Test Methods

Approximate 0.5 kg quantities the pure energetics, shown in Table 2, were burned inside the chamber in each test. The material was remotely ignited and the combustion process was allowed to go to completion with no personnel intervention. Continuous and volume-integrated samples of emissions products were collected during each of the tests using sampling methods more fully described below.

Table 2 Description of Typical Pure Energetics Selected for Emissions Testing

Energetic	Ingredients (Weight Percent)
Composite Propellants	Ammonium Perchlorate (85-86) Polymer Binders (13-14) Metal Salts (≤1)
Aluminized-Composite Propellants	Ammonium Perchlorate (55-75) Aluminum (10-22) Polymer Binders (9-17) Nitramines (0-14) Metal Salts (≤1)
Double Base Propellants	Nitramines (60-64) Nitrate Esters (24-26) Polymers (6-8) Metals/Metal Salts (2-4)
Plastic-Bonded Explosives	Nitramines (82) Polymer Binders (12) Plasticizers, Metals etc. (6)

3.1 Gases

CO_2 - Carbon dioxide was measured using a continuous infrared gas filter correlation analyzer. These data were used in the application of the carbon balance method (discussed in more detail below) to calculate emission factors for a subset of target pollutants.
CO - Carbon monoxide was measured using a continuous infrared gas filter correlation instrument and by evacuated canister and gas chromatography analysis. Carbon monoxide was also used in the application of the carbon balance method to these test burns.
NO-NO_2 - Nitrogen oxides were measured using a continuous chemiluminescent analyzer.
HCl - Hydrogen chloride measurements were carried out in the chamber during tests of chlorine-containing composite propellants using open-path fourier transform infrared spectroscopy (Open Path FT-IR). The open-path FT-IR method is an *in situ* sampling approach that avoids many of the sampling loss problems that occur with extractive sampling methods for reactive species such as HCl.
NH_3 - Quantitative measurements of ammonia as a potential product of combustion from composite propellants was also available from the FT-IR spectrum collected during the tests and from bubbler sampling systems accompanied by lab colorimetric analysis.

3.2 Vapors

Total Non-methane Hydrocarbons (TNMHC) - Total organic vapors were collected in evacuated, passivated (SUMMA®) canisters and analyzed by gas chromatographic methods using EPA TO-12 analysis guidelines[1].
Toxic Volatile Organic Compounds - Analysis of the EPA-designated, 42-compound list of potentially toxic volatile organic compounds was carried out on canister samples using GC-MS analysis procedures outlined in EPA TO-14[2].

3.3 Aerosol

PM_{10} - Aerosol emissions from all test burns in the chamber were measured with a high volume sampler equipped with a PM_{10} sampling head. The methodology included gravimetric analysis of the filters before and after sampling.
Semi-Volatile Organic Compounds - Semi-volatile organic samples were collected on a modified pesticide sampling unit using pre-fired quartz filters and a XAD-2 resin cartridge. No size differentiation was employed in this sampler; thus, total aerosol and associated vapors were collected on the filter and backup resin cartridge. In the laboratory, solvent extraction was used with GC-FID and GC-MS-Ion-Trap methods to screen for a wide range of potentially toxic semi-volatile organics. A dioxin screening analysis was also carried out on the same sample extract using similar GC-MS methods.
Heavy Metals - Since many of the propellants to be tested contain heavy metal salts as burn modifiers, an analysis for elements such as Pb, Fe, Bi, Sn, Zr, Mo was also carried out. A total aerosol sample was collected on a Teflon filter and analyzed by x-ray fluorescence techniques. An analysis for aluminum by inductively coupled plasma atomic absorption spectroscopy was also carried out since it cannot be detected by x-ray fluorescence methods.
Total Nitrate - A nylon filter and intermediate flow pump was used to collect a total nitrate sample during the pure propellant burns. Sample collection was followed by ion chromatographic analysis in the laboratory for total water soluble nitrate.
Total Chloride - A low flow bubbler system that included a mixed cellulose ester filter followed by two midget glass impingers connected in series and filled with 0.1 N sulfuric acid was used to collect total chloride aerosol and ammonia. Laboratory analysis included mercuric nitrate titration of the filter extract for total chloride and colorimetric analysis of the bubbler solutions for ammonia content.

3.4 Emission Factor Calculations

Target pollutant emission factors were determined by one of two methodologies applied to the data set obtained from the SNL chamber tests. The emission factor is defined here as the total mass yield of a particular pollutant expressed as a fraction of the starting mass of waste material that undergoes burning.

3.4.1 Emission Factor by Volume Method

Sampling of pollutants was conducted from a homogeneous mixture inside the chamber. Since the internal volume of the chamber is known, the total mass of a particular pollutant can be estimated for any particular burn scenario. The emission factor can be calculated by the following:

$$EF_x = \frac{[X] \bullet V}{M}$$

In this expression, EF_x is emission factor of the pollutant species of interest (μg/kg), [X] is the concentration of species x measured in the chamber following the burn (μg/m^3), V is the volume of the chamber (m^3) and M is the original mass of waste material (kg). In this calculation we assume minimal reactivity of the target pollutants with the interior surfaces of the chamber. While surface effects can never be eliminated, they are judged to be of limited importance since the chamber's internal volume to surface ratio is reasonably large, thus minimizing the interaction of the chamber contents with the chamber walls. A possible exception in this case is the quantitative determination of reactive gaseous species such as hydrogen chloride. Special considerations for HCl are described in a following section of this paper.

3.4.2 Emission Factor by Carbon Balance

An alternative approach for the determination of emission factors involves the use of total carbon in both aerosol and gaseous form as a tracer of total waste mass. Provided that the carbon mass fraction of the starting waste material is known, the concentration of any particular pollutant can be ratioed against the total carbon measured in the same volume of air sampled from the chamber. This technique assumes that both aerosol and gases move together as effluents in the plume, experiencing the same mixing and dilution phenomenon. The expression used to determine the emission factor of a particular pollutant is as follows

$$EF_x = F_c \bullet \frac{[X]}{[C_{tot}]}$$

where EF_x is the emission factor of species x, F_c is the carbon fraction of the starting material, [X] is the concentration of the species of interest in the collected sample and $[C_{tot}]$ is the concentration of total carbon in the same sample. The carbon balance method is more versatile than the mass balance approach since a fully-mixed chamber is not required for its application. The carbon balance method compared well with the mass balance technique under a controlled test pollutant emissions from both detonation and burning of energetic materials[3].

3.5 Data Processing Procedures and Calculations

On selected tests, a known volume of pure SF_6 gas was released into the chamber immediately prior to the burn test. The concentration of the tracer gas was then continuously monitored by an open-path FT-IR. The mass concentration of tracer gas was determined from the spectral data and used to derive the total volume of the chamber. Repeated tracer gas measurements yielded a chamber volume of 784 m^3 with an uncertainty of 2%. Analysis of each volume-integrated sample provided a measure of the total mass of a particular species on the collection medium. Calculation of the emission factor for each pollutant type was carried out using either the volume method or the carbon balance method as described earlier. A dilution correction factor, derived from the measured decay rate of the SF_6 tracer gas, was used to account for chamber leakage encountered over the sampling time interval. Typically, this correction factor was in the range of 10 to 20 percent for the 1 to 2-hour sampling intervals employed in this study.

The time series data from continuous or quasi-continuous monitors such as the gas instruments and the FT-IR was used to extrapolate the total mass release of the species of interest inside the chamber. Earlier testing in the chamber has shown that exponential decay laws accurately describe the dilution characteristics of the chamber, provided that the chamber volume is continuously mixed. Exponential decay theory reveals that a plot of the log of the concentration of a particular species with elapsed time yields a linear plot with the intercept at zero-time (the time at which emissions cease) being equal to the virtual mixed concentration of the gas at the completion of the burn. In practice, the contents of the chamber are not fully mixed over the first ten minutes following burn completion; however, tracking gas data continuously over a 1-hour interval allows extrapolation of the data back to zero-time with acceptable accuracy. The product of this derived zero-time gas concentration and the building volume yields an estimate of the total mass release of each gas following the test burn. Emission factors were determined as described in the previous paragraph by ratioing the total mass release of each gas to the starting mass of the test material.

4. Gas and Aerosol Emission Factors

Target analyte emission factors for the pure energetic materials tested in the chamber are given in Table 3 for gases and vapors and in Table 4 for semi-volatile organic and heavy metal aerosols. The emission factor given is the highest of two measurements made on each material. Emission factors were calculated by the chamber volume method, as described above, for all species except volatile organic compounds collected in the steel canisters, for which the carbon balance method was used.

Table 3 Gas and Volatile Organic Compound Emission Factors for Pure Energetics

Chemical Species	Emission Factor (g/kg)			
	Al-Composite	Composite	Double Base	PBX
CO	< 2.0E-1	1.2E-1	3.0E+0	2.9E-1
NO	3.6E+0	4.0E+0	2.3E+0	2.4E+0
NO_2	5.9E-1	5.9E-1	1.9E-1	3.1E-1
SO_2	4.0E-1	1.0E-1	4.1E-2	1.4E+0
NH_3	<5.7E-1	<1.6E-2	<5.7E-1	<5.7E-1
TNMHC[a]	<2.7E-2	4.3E-2	4.0E-2	5.8E-2
n-Hexane	<1.6E-2	<2.2E-2	<4.5E-3	<3.1E-3
1,3 Butadiene	<1.6E-2	<2.2E-2	<4.5E-3	<3.1E-3
Benzene	1.1E+0	1.5E-1	2.1E-2	<3.1E-3
Toluene	1.6E-2	1.1E-1	<5.3E-3	<3.1E-3
Styrene	<1.6E-2	<2.2E-2	<5.3E-3	<3.1E-3
Xylenes (o,m,p)	<1.6E-2	8.6E-2	<5.3E-3	6.2E-3

Notes: [a] TNMHC = Total Non-Methane Hydrocarbons

5. Hydrogen Chloride Gas Measurements

We made a special effort in this test series to measure hydrogen chloride emissions from test burns of two composite propellant formulations containing ammonium perchlorate with and without aluminum additive. For these measurements, an open path FT-IR spectrometer was used inside the chamber so that *in situ* measurements could be carried out. The spectrometer was operated in a bi-static configuration, with a hot filament source and parabolic reflector positioned at one end of the chamber and an interferometer/detector unit at the other end of the chamber, resulting in a total beam pathlength of 12.5 m. The spectrometer was operated at a resolution of 2 cm^{-1} and 32 spectra were co-added into each interferogram. A background or reference spectrum was collected just prior to ignition of the propellant. Interferograms were collected over a 15-second interval every minute for about 50 minutes following the start of each burn. In the bi-static configuration of this particular spectrometer, the source radiation is not modulated through the interferometer. Consequently, the background (source off) blackbody radiation must be taken into account when doing quantitative measurements. A single beam spectrum

Table 4 Semi-volatile and Aerosol Emission Factors for Pure Energetics

Chemical Species	**Emission Factor (g/kg)**			
	Al-Composite Propellant	**Composite Propellant**	**Double Base Propellant**	**PBX Explosive**
PM-10	5.7E+1	4.8E+0	1.1E+1	5.3E+0
Total Nitrate	5.3E-2	4.6E-2	2.5E-2	5.3E-2
Aluminum	1.0E+2	NA	NA	NA
Lead	NA	NA	8.8E+0	NA
Zirconium	NA	8.8E+0	8.8E+0	NA
Copper	NA	NA	NA	4.0E+1
Molybdenum	NA	NA	NA	NA
Iron	NA	NA	NA	1.1E-2
Mesitylene	3.3E-5	5.9E-5	8.4E-5	3.0E-4
Phenol	<2.8E-3	2.8E-3	2.3E-4	6.2E-4
Naphthalene	1.1E-3	3.9E-3	7.1E-5	2.5E-4
Thianaphthene	<9.0E-5	<8.5E-5	<5.4E-5	2.9E-4
Resorcinol	5.5E-3	2.3E-3	6.0E-3	1.2E-3
2-Methylnaphthalene	8.6E-3	9.3E-3	5.9E-3	<6.5E-3
1-Methylnaphthalene	2.4E-3	9.0E-4	1.2E-4	<4.8E-4
Tracetine	<9.0E-5	<8.5E-5	<5.4E-5	<4.9E-5
Biphenyl	4.7E-3	1.0E-3	1.9E-4	1.3E-3
2,6-Dinitrotoluene	7.2E-6	5.8E-3	4.7E-3	5.4E-3
Dibenzofuran	1.0E-3	6.9E-4	1.7E-4	1.4E-4
4-Nitrophenol	<9.0E-5	<8.5E-5	<5.4E-5	<4.9E-5
2,4-Dinitrotoluene	<9.0E-5	5.8E-3	<5.4E-5	<4.9E-5
Di-n-propyl adipate	<2.7E-3	<2.7E-3	<9.5E-4	9.0E-4
Diphenylamine	1.9E-4	<1.9E-4	<1.4E-4	1.4E-4
2-Nitronaphthalene	<5.4E-4	1.7E-3	2.3E-4	3.8E-4
Phenanthrene	2.0E-3	2.9E-4	3.5E-4	1.1E-4
2,5-Diphenyloxazole	9.5E-4	4.3E-7	1.7E-4	2.5E-4
N-Nitrosodiphenylamine	<9.0E-5	<8.5E-5	<5.4E-5	<4.9E-5
Pyrene	<9.0E-5	<8.5E-5	<5.4E-5	<4.9E-5
4-Nitrosodiphenylamine	<9.0E-5	<8.5E-5	<5.4E-5	<4.9E-5
Benz[a]anthracene	<9.0E-5	4.4E-3	3.3E-3	<3.3E-3
1-Nitropyrene	<4.4E-3	<8.5E-5	<5.4E-5	<<4.9E-5
Benzo[a]pyrene	<9.0E-5	<8.5E-5	<5.4E-5	<4.9E-5
1,6-Dinitropyrene	<9.0E-5	<8.5E-5	<5.4E-5	<4.9E-5
Dibenz[a,h]anthracene	<9.0E-5	<8.5E-5	<5.4E-5	<4.9E-5
Dioxins	<6.5E-4	<6.5E-4	<4.9E-4	<4.9E-4

Notes: NA = no analysis

was collected with the infrared source off under the same instrument collection conditions used during the test. This spectrum was digitially subtracted from all reference and test spectra prior to further spectral processing.

The test spectra were ratioed against the reference spectrum to produce a plot of absorbance as a function of wavelength in the spectral region ranging from 700 to 4000 cm^{-1}. A typical test spectrum before and after propellant ignition is shown in Figure 3. A sharp absorption feature at about 945 cm^{-1} is from the SF$_6$ tracer gas and can be observed in the spectrum taken after propellant ignition. A cluster of peaks in the 2700-3100 cm^{-1} region of the spectrum is associated with HCl gas released after propellant ignition. The multiple-peak absorption feature in the 2350 cm^{-1} region is associated with carbon dioxide release during the burn.

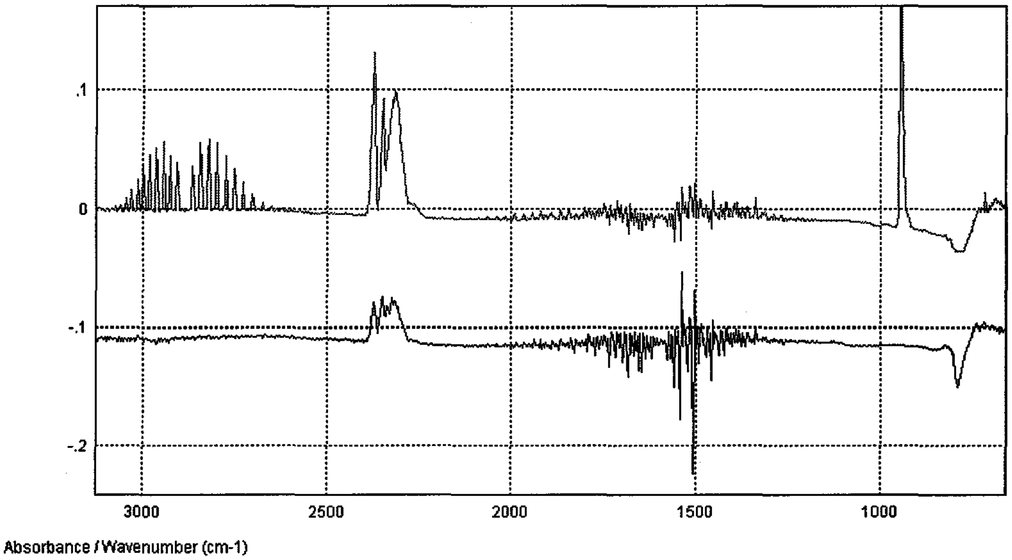

*Figure 3 FT-IR Spectrum of chamber air before **(lower)** and after **(upper)** a Composite Propellant Burn*

Quantitative analysis of both SF_6 and HCl in the FT-IR spectra was carried out by integrating the absorbance of a selected absorption peak for both species and comparing this result to calibration spectra produced either on site in a long-path cell or obtained from a commercial provider of digitized spectra (Infrared Analysis, Inc., Anaheim, CA). Spectral data were collected at about 1,500 m msl in Albuquerque, NM at an ambient pressure of about 0.82 atm., whereas the HCl calibration spectra was taken at standard conditions of pressure and temperature. A correction term, derived from ambient pressure and temperature measurements during the test, was used to correct for air density differences between calibration and test conditions. Hydrogen chloride spectral features are expected to be narrower at lower pressures as a result of diminished pressure broadening effects on spectral line width. The spectral features are narrower than the spectrometer resolution at both test and standard pressures. Consequently, under either condition, the entire spectral feature is integrated by the spectrometer such that line width changes from pressure changes will not influence the quantitative result. The overall accuracy of the HCl spectrum is estimated to be ±20%[5].

A plot of HCl and SF_6 concentrations in the chamber as a function of elapsed time is shown in Figure 4 for a Composite/Al and a Composite burn. The chamber dilution caused by the inflation blower is tracked by the SF_6 decay and is on the order of about 10% per hour. The HCl decay rate is higher than that observed for SF_6 however, as evidenced by the steeper slopes of the HCl plots.

The release mass of a species can be inferred from these time series measurements by extrapolating the decay curve back to zero elapsed time following burn completion. The product of the zero-time concentration and the chamber volume yields a measure of the total mass of the species released into the chamber. In theory and in practice, a plot of the log of the gas concentration versus time yields a straight line for a mixed chamber system with a constant leak rate. Regression data for log-transformed HCl and SF_6 data are given in Table 5, revealing a good linear fit as evidenced by R^2 values generally in excess of 0.99. Since SF_6 is inert, its decay rate and associated concentration half-life is a measure of the leak rate of the chamber. For these tests the concentration half-life was on the order of 200 minutes. As can be noted in Table 5, the HCl concentration half-life is on the order of 20-40 minutes, nearly an order of magnitude lower than that observed for SF_6. This observation reveals that gas phase HCl is disappearing at a higher rate than would result from chamber leakage alone. We suggest that irreversible absorption of HCl is occurring on (1) the chamber surfaces; and, (2) suspended particulate matter in the chamber, causing the higher HCl decay rate.

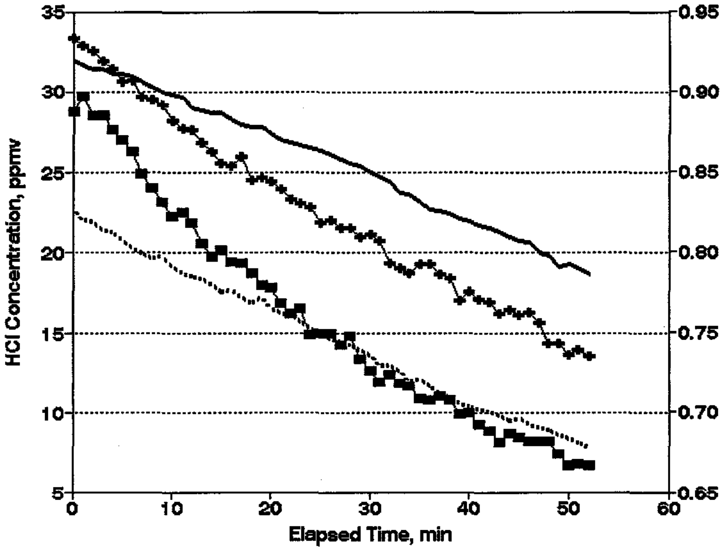

Figure 4 Hydrogen chloride and SF_6 concentrations in the chamber for Composite-Al and Composite Burns. ***Solid square,*** *HCl from Composite/Al;* ***Cross,*** *HCl from Composite;* ***Solid Line,*** *SF_6 from Composite/Al;* ***Dotted Line,*** *SF_6 from Composite*

Table 5 Tracer gas and HCl Regression Data and Emission Factors

Parameter	Test 1 Composite/Al	Test 2 Composite/Al	Test 3 Composite	Test 4 Composite
Zero-time HCl Conc., ppmv	48.2 ± 1.0	31.0 ± 1.0	37.2 ± 1.0	33.9 ± 1.0
HCl Concentration Half-Life, min	20	24	25	41
SF_6 Concentration Half-Life, min	167	318	218	211
HCl Regression Linearity (R^2)	0.980	0.991	0.995	0.986
SF6 Regression Linearity (R^2)	0.982	0.980	0.994	0.892
HCl Emission Factor - Experimental (g HCl / g Propellant)	0.14	0.12	0.14	0.13
Total Cl Emission Factor - Theoretical (g/g)	0.22	0.22	0.26	0.26

The time series data reveal that HCl adsorption/loss rate is constant over the regression interval. The zero-time HCl concentrations, obtained by extrapolation of the log-transformed data, are shown for all four tests in Table 5. In the regression analysis, we ignored the first ten minutes of data following the burn since the chamber is not fully mixed during this interval. The time-zero HCl concentration, the chamber volume and the starting mass of propellant are used to calculate an HCl emission factor for each of the four tests that were conducted. The experimental HCl emission factor and the total Cl emission factor are also given in Table 6. The theoretical total Cl emission factor is based on the total mass fraction of chlorine in the propellant mix. The ratios of experimental to theoretical emission factor for the four tests fall in the range of 0.51 to 0.64 suggesting that all chlorine in the propellant cannot be fully accounted for by the HCl gas measurements in the chamber.

6. Discussion

6.1 Gas and Vapor Emissions

Results from these experiments show that during combustion, the pure energetics produce little gas other than carbon dioxide. Carbon monoxide emission factors are in the range of 0.01 to 0.3 percent (0.1 to 3 g/kg) with the highest emissions observed for the double base and explosive. The molar ratio of CO to CO_2 was very low indicating a high degree of combustion efficiency, which is expected, given the near 100% oxygen balance that these materials posses. Nitrogen oxides (NO and NO_2) emissions generally fall in the same range as observed for CO with NO_2 emissions about an order of magnitude less than NO emissions. Sulfur dioxide is detected, however only at very low levels since sulfur species only occur in these formulations as trace level contaminants. Hydrocarbon emissions, represented by total non-methane hydrocarbons and selected species such as hexane and benzene, are either non-detectable or at very low levels further illustrating the relatively clean nature of these burns.

6.2 Semi-Volatile Hydrocarbon and Aerosol Emissions

Although a few species in a pre-established target analyte list, shown in Table 4, were detected in the pure energetic burns, no clear trend was observed in the measurements with regard to energetic type. In general, emission factors for these potentially toxic compounds were at or below 1 mg/kg and in many cases non-detectable at an emission level of about 0.1 mg/kg. These data are important in the risk assessment process since the carcinogenic species with low risk based concentrations generally fall into this pollutant category. Aerosol emissions, represented by PM_{10} measurements were in the range of about 0.5 to 5 percent with the highest emissions observed for the aluminized composite propellant.

6.3 HCl Emissions

Hydrogen chloride gas measurements via open-path FT-IR reveal that about 50% of the total chlorine in the composite propellants is detected as gaseous HCl following a burn. Early studies by Dode' and Bircumshaw *et al* concentrated on the decomposition products of ammonium perchlorate and showed that nitrogen, water, oxygen, nitrous oxide, hydrogen chloride, nitrosyl chloride, nitrogen trioxide and nitrogen dioxide are produced at temperatures less than 300 C[5,6]. Rosser *et al* have carried out quantitative analysis of gaseous emission products from ammonium perchlorate and report emission factors of 0.23 g/g for chlorine and 0.05 g/g for hydrogen chloride at a decomposition temperature of 275 C[7]. Major gaseous reaction products from ammonium perchlorate decomposition at higher temperatures are postulated to be chlorine, water, nitrous oxide, nitric oxide and oxygen[8]. On the basis of these observations, we suspect that the balance of the chlorine mass, not detected as hydrogen chloride in these chamber tests, is present as chlorine gas. Chlorine gas is not infrared active and cannot be detected by FT-IR methods. Total chloride analysis of the filter/bubbler sampling train showed levels approximately one-half of the equivalent total chloride observed with the FT-IR system. No aerosol chloride was detected with this method. The filter/bubbler system, which was optimized for ammonia gas collection, did not quantitatively collect HCl gas, thus resulting in the observed negative bias of the method. If, as we suspect, chlorine gas accounts for the balance of original chlorine in the propellant, its emission factor would be 0.11 ± 0.02 g/g , as determined by the difference between total chloride in the propellant and measured HCl.

7. Summary and Conclusions

Emission characterization studies involving a double base, composite propellants and a plastic bonded explosive reveal that with the exception of inorganic chlorine species, low to non-detectable amounts of gases, volatile organics and semi-volatile organic aerosols emissions are released during burning of these materials under ambient pressure conditions. Potentially toxic organic species are generally non-detectable at an emission factor level of about 1 µg/g. Incomplete combustion product gases such as carbon monoxide and nitrogen oxides were detected at low levels, with emission factors in the range of 3×10^{-3} to 3×10^{-4} g/g. When the low emission factors, such as encountered in this study, are folded into a typical large-scale burn scenario incorporating a dispersion model, the predicted off-site inhalation hazard impacts are typically not significant. Such results may warrant a limited policy of selected energetics disposal by open burning under appropriate atmospheric conditions. Inorganic chloride species are released from composite propellants containing ammonium perchlorate in the form of both hydrogen chloride, as detected by open path FT-IR, and chlorine gas on the basis of earlier characterization work. In this study, we report hydrogen chloride emission factors in the range of 0.12 to 0.14 g/g. Although chlorine gas was not reliably sampled in this work, we infer an emission factor of 0.11g/g if the assumption is made that the mass deficit between total chlorine in the propellant and that detected as hydrogen chloride is in the form of gaseous chlorine. No aerosol chloride was detected in these tests, further suggesting that all chlorine combustion products are in the gaseous phase. In light of the toxicological similarities between hydrogen chloride and chlorine gas, it may be acceptable to assume that all chlorine in ammonium perchlorate propellants is released as hydrogen chloride for the purposes of quantitative air pathways health risk assessments.

8. Acknowledgments

This work was funded by the US Navy, Sea Systems Command as a component its overall contract with Alliant Techsystems. We acknowledge the work of Dr. R. A. Rasmussen and staff at the Oregon Graduate Institute in Beaverton OR; Dr. Bob Wright and staff and Battelle Pacific Northwest Laboratories in Richland, WA ; Mr. Robert Giaque at the Lawrence Berkeley Laboratory in Berkeley, CA; and, Mr. Charles Gray as Sandia National Laboratories for their capable work in laboratory analysis of the various samples.

9. References

1 "Method for the Determination of Non-Methane Organic Compounds in Ambient Air Using Cyrogenic Preconcentration and Direct Flame Ionization Detection," in Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, June 1988, EPA Publication No. EPA/600/4-89/017, US EPA, Office of Research and Development, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC 27711.

2 "Determination of Volatile Organic Compounds in Ambient Air Using Summa® Passivated Canister Sampling and Gas Chromatographic Analysis," in Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, June 1988, EPA Publication No. EPA/600/4-89/017, US EPA, Office of Research and Development, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC 27711.

3. Einfeld, W., D. J. Morrison, and B. V. Mokler, 1990. "An Experimental Study to Determine Gaseous and Particulate Products From Small-Scale TNT Detonations and Propellant Burns," Report No. SAND90-0605, Sandia National Laboratories, Albuquerque, NM 87185.

4. Phil Hanst, Infrared Analysis Inc., Anaheim, CA 92801, Personal Communication

5. Dode′, M., 1938. Bull. soc. chim. France [5], 5, 170.

6. Bircumshaw, L. L. and B. H. Newman, 1955. Proc. Roy. Soc. A 227, 115, 228.

7. Rosser, W. A., S. H. Inami and H. Wise, 1968. Comb. & Flame 12, 427.

8. Urbanski, T., 1964. Chemistry and Technology of Explosives, Volume 4, Pergamon Press, New York, pp 440-450.