Efficiency of Perchlorate Consumption in Road Flares, Propellants and Explosives

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Abstract

When an explosive detonates or a propellant or flare burns, consumption of the energetic filler should be complete but rarely is, especially in the presence of large amounts of non-combustible materials. Herein we examine three types of perchlorate-containing devices to estimate their potential as sources of contamination in their normal mode of functioning. Road flares, rocket propellants and ammonium nitrate (AN) emulsion explosives are potentially significant anthropogenic sources of perchlorate contamination. This laboratory evaluated perchlorate residue from burning of flares and propellants as well as actual detonations of ammonium nitrate emulsion explosives. Residual perchlorate in commercial products ranged from 0.094 mg perchlorate per gram material (flares) to 0.018 mg perchlorate per gram material (AN emulsion explosives). The rocket propellant formulations, prepared in this laboratory, generated about 0.014 mg of perchlorate residue per gram of material.

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1. Introduction

Perchlorate (ClO_4^-) is an oxidizing anion that has been found in ground and surface waters throughout the United States (U.S.). In these natural aqueous systems, perchlorate is both extremely mobile and persistent since it adheres poorly to mineral and organic materials and is inert in aerobic environments.[1] There is some debate as to sources of perchlorate in the environment. Natural sources include lightning discharge[2] and is evident from mineral deposits containing high concentrations of perchlorates such as Chilean caliche.[3,4] Grenades, mortars, and propellants used to fuel rockets and missiles are often singled out as significant anthropogenic sources of perchlorates. However civilian devices such as road flares, blasting agents, and fireworks contain ample amounts of perchlorate.[5] Further, the chemical industry is responsible for roughly 568 short tons [515 metric tons(mt)] of sodium perchlorate (formed or imported) each year as a by-product of the synthesis of sodium chlorate, used in the pulp and paper industries.[6]

Although there are currently no enforceable limits for perchlorate contamination, the Environmental Protection Agency (EPA) has become increasingly concerned about the possible risk to public health due to perchlorate contamination of ground water. In early 2005, a National Academy of Sciences (NAS) study indicated that at sufficiently high doses, perchlorate could interfere with the production of thyroid hormones by decreasing the uptake of iodide by the thyroid gland.[5] In February of 2005, the EPA established an official "reference dose" - the daily exposure level that is safe for humans – for perchlorate in accordance with the findings of the NAS study.[1] Currently, this proposed threshold stands as 0.0007 mg/kg-day, which translates to a maximum value of 24.5 ppb (µg/L) in drinking water. However, several states have set their own maximum allowable perchlorate levels for drinking water; these include Massachusetts (2 ppb), California (6 ppb), New Jersey (5 ppb), and Arizona (14 ppb).[7]

Interestingly, other anions, such as nitrate, also inhibit iodide uptake, although much less effectively than perchlorate. Nitrate has been estimated to be 1/240th as effective as perchlorate in this regard; however, nitrate also tends to be present in the environment at levels that are several orders of magnitude higher than those of perchlorate.[8] The reference dose for nitrate is 0.16 mg/kg-day (sometimes reported as 0.1 mg/kg-day and based on a 4-kg infant drinking 0.64L of water per day). The maximum allowable nitrate level in drinking water is 44 mg/L (nitrate) or, as it is most often reported, 10 mg/L (nitrate nitrogen).[9] These standards have nothing to do with iodide suppression; they are based on the risk factor for infants developing methemoglobinemia as the result of high nitrite concentrations in their blood. In an infant's gastrointestinal tract, bacteria convert nitrate to nitrite, which can result in the formation of methemoglobin (Me-Hb). Because newborns have fewer enzymes that are capable of converting Me-Hb to Hb, they are at risk for methemoglobinemia while healthy adults are not (assuming drinking water levels do not exceed 100-200 mg/L nitrate nitrogen).[10]

As legal limits for perchlorate are established, it is imperative that measures be taken to identify sources of environmental perchlorate. Since the 1940's, one of the major uses of perchlorate has been for ballistic rocket motors. From total purchase records of the Department of Defense (DoD) and National Aeronautics and Space Administration (NASA), it has been estimated that 20 million pounds (~9,000mt) of ammonium perchlorate have been used annually for that purpose.[11] More recently perchlorates have been used in select commercial ammonium nitrate-based emulsion explosives to supplement the energy released. In addition, many formulated ammonium nitrate explosives use sodium nitrate from naturally occurring deposits in Chile. These are estimated to have a small (0.2%) amount of perchlorate contamination.[3,12] Although the widespread contamination of the environment due to road flares may seem unlikely, it is reported that more than 40mt of flares were burned in a single county in California in 2002.[13] This copious use, combined with the fact that perchlorate may account for as much as 10% of the filler material in the flare, suggests that flares may contribute significantly to perchlorate pollution.[14]

When an explosive detonates or a propellant or flare burns, consumption should be complete but rarely is, especially in the presence of large amounts of a non-combustible material. Herein we examine three types of perchlorate-containing devices to estimate their potential as sources of contamination in their normal mode of functioning.

2. Materials and Method

2.1 Explosives

2.1.1 Preparation of Charges

Two Orica brand ammonium nitrate emulsion explosives (MagnaFrac and Apex Elite) were purchased. Although the MSDS suggested that sodium perchlorate (NaP) would be present in each, analysis showed only trace amounts (see "as received" amounts for each explosive in Table 1). Accordingly, anhydrous NaP (ACS-certified) purchased from Fisher was added to the commercial emulsion explosives at approximately 5 wt% and 10 wt% levels. Mixing was accomplished by hand kneading. A third Orica ammonium nitrate emulsion explosive, MagnaUltra, was later supplied by Orica; as it contained 7 wt% NaP blended in by the manufacturer, no additional perchlorate was added. The first two emulsions were tested in November 2006 and the last emulsion in May 2007. To the extent possible, experimental conditions were kept the same. Charges of about 500g were placed in polystyrene foam containers; the top of each container was covered with duct tape and wire was laced through the sides to hang the container in the center of the room. A detonator, either EB#7 or EB#11, was inserted in each container by puncturing a hole through its base.

2.1.2 Preparation of Test Chamber and Detonations. *Spiked Samples.* The test chamber for the first set of ten charges (MagnaFrac and Apex Elite) was a free-standing 3.05m x 3.05m x 2.29m (10 ft wide x 10 ft deep x 7.5 ft high), steel-reinforced concrete building. There was a standard-size open doorway in the south wall, a large window containing no glass in the west wall, and a chimney hole east of the center of the room. The room was washed with tap water, and plywood was attached to each of the four cement walls using glue or caulk and cement nails. Perchlorate was not detected in the tap water (detection limit 0.3 ppb or 0.3 μg/L) prior to washing but a trace amount of perchlorate (about 2.7 ppb) was detected following washing prior to testing. Initially (shots 1-5), the door and window openings were not covered; for shots 6-10, due to wind, the openings were covered with free-standing plywood panels.

On the first shot, the foil partially covered two walls and the floor; for all other shots two walls and the floor were totally covered. Strips of aluminum foil [1.22m x 0.46m and 0.91m x 0.46m (4 ft x 1.5 ft and 3 ft x 1.5 ft)] were stapled to the plywood of the designated walls; the floor was covered with larger [3.05m x 0.46m (10 ft x 1.5 ft)] pieces of foil, which were anchored with rocks or bricks. Thus, approximately 48% of the total interior surface of the building was covered with aluminum foil. After the room had been prepared as described, the polystyrene foam container of emulsion explosive was hung upside down in the center of the room about 1.07 to 1.22m (3.5 to 4 ft) above the floor. Personnel were evacuated, and the shot was initiated. Collection of the shredded witness foil began immediately after firing; foil from inside the building, as well as along the outside perimeter, was collected. Once all but the smallest pieces of foil had been picked up by hand, the floor was swept. Despite the care taken, not all the foil was recovered; the losses were estimated to be about 6% in all cases. The foil collected from each shot was compacted into a single 121L (32gal) plastic bag. The ten bags were shipped to the URI lab for analysis.

As-received Samples. The building used for the first ten spiked charges was so badly damaged that a new test chamber was used for the three Magnum Ultra shots. The new building was a free-standing 2.44m x 2.44m x 2.13m (8 ft wide x 8 ft deep x 7 ft high), steel-reinforced concrete lean-to with only three walls. The building was not washed prior to covering. The floor, ceiling, and three walls were covered with plywood panels. Aluminum foil was stapled to the rear wall, one side wall, and the ceiling, and laid on the floor. This time, the coverage was approximately 64% of the internal surface of the building. Percent foil recovered from each shot (93-94%) was calculated by weighing recovered foil and comparing that to the calculated amount used. Between shots, the building was swept, but not washed.

2.1.3 Analysis of the Aluminum Foil

The aluminum foil was subjected to a three-step water rinse. Each piece of foil was unfolded, placed in 3L of doubly-distilled deionized (DDD) water, and agitated for about five seconds. After the excess water was shaken from the foil, it was placed in a second aliquot of 3L of DDD water where the washing process was repeated. This was followed by a third aliquot, after which the foil was shaken dry and set aside or discarded. A small net was used to hold and wash the smallest pieces of foil.

Once all the foil from a single shot was washed, the water from each of the three rinses was filtered using Whatman #41 filter paper and then weighed. The walls and lids of the containers were scrubbed and rinsed with DDD water to ensure that all residues were removed. The water from scrubbing was added to the rest of the wash water. Once the exact mass of each of the three rinse solutions was known, 125-mL Nalgene bottles were filled with each solution and sent out for analysis. This procedure was performed for nine of the shots (shots 1-3 and 5-10). For the remaining four shots (4, 11, 12, and 13), the three rinses were combined at the last step and thoroughly mixed, and only one sample (125mL) was sent for analysis. In almost all cases, the rinse solutions were analyzed via EPA methods 314 (perchlorate) and 300.0 (nitrate); the results are shown in Table 2.

2.2 ROCKET MOTORS

Several formulations of ammonium perchlorate (AP) "rocket motors" were prepared (see Table 3) using guidance from the literature.[15] Both hydroxyl-terminated polybutadiene (HTPB) and carboxy-terminated polybutadiene (CTPB) were used as the polymer base. In order to control the viscosities and burn rates of the motors, AP of two different grain sizes (300 and 90 microns) was used. Both aluminized (Al) and non-aluminized motors were made and tested; addition of the aluminum caused the propellant to change color from white to gray. Initially, the motors prepared were small (~30g) and cast in a roll of heavy paper. If the paper was not removed before burning of the motor, some charred paper residue remained; when the paper casing was removed prior to the burn, no residue was visible. A large (26cm x 36cm) enamel-coated steel pan covered in aluminum foil was used to collect residue from the burns. Motors were held above the pan, either vertically or horizontally, by use of a clamp; the pan was carefully positioned under the motors so that the residue from the burn was collected. In one burn, the motor was placed on a bed of sawdust in the pan. At the end of each burn, the pan and aluminum foil were thoroughly rinsed with DDD water, and a portion of that solution was sent for analysis.

Later, larger rocket motors (~24.3cm long and 7.7cm diameter, weighing about 1.7kg) were prepared and burned outside in a small brick chimney. A piece of plywood (31cm x 71cm) was used as the platform on which the brick chimney (19cm x 5.6cm x 9.2cm) was built (a rectangle two bricks long, one brick wide and three bricks high), leaving an interior floor space about 12cm x 36cm, which was covered with sandbox sand (approximately 5-7kg). The rocket motors were placed on the sand and lit by means of a paper wick. The burn typically lasted about two minutes. The chimney was allowed to cool and the bricks were rinsed with DDD water, resulting in the collection of 1-2L of a water/sand solution. The sand used to cover the plywood was also collected and brought back to the laboratory, where it was placed in a 18.9L (5gal) bucket and covered with 1-2L of DDD water. After mixing for three minutes, the water was decanted into a filter. This process was repeated two additional times. After the third time, the sand collected by the filter paper was rinsed. All filtered water from the workup (5-6L) was poured into a 6L Erlenmeyer flask, where it was thoroughly mixed. A sample was placed into a 125-mL Nalgene bottle and sent to an outside lab for analysis by EPA method 314. It was estimated that the sand retained between 0.35L and 0.5L of water. Rocket motor burn details are in Table 4.

2.3 FLARES

Road flares differ markedly from propellants and are used more widely. Though flares have about one-tenth the perchlorate content of the propellants, flares are often cast aside before the burn is complete. In this study, flares were examined to determine whether perchlorate concentration was uniform throughout a flare, and to determine how much perchlorate flares contained before burning and after burning. In North America, there is only one flare manufacturer - Orion. For comparison, flares were also acquired from National Flare Company and marked “made in China.” Orion flares examined were 15-minute flares dated July or September 2005; the Chinese flares were 30-, 20-, 15-, 10-, and 5-minute flares.

Analyses of Unburnt Flares. To establish the uniformity of perchlorate concentration throughout the flare, several flares were sectioned into three equal pieces. Four grams of filler material was removed from each section and diluted to a volume of approximately 300mL with DDD water. The resulting solution was heated to a temperature in the range of 70-80^{o}C and stirred for ten minutes; it was then allowed to cool to room temperature before being brought to a final volume of 500mL by the addition of more DDD water. An aliquot of the solution was filtered through a syringe filter into a LC-autosampler vial to be analyzed.

Analyses of Burnt Flares. Each flare was weighed and positioned horizontally in a clean pan, which was placed on top of and surrounded by fresh sheets of aluminum foil. The flares were ignited using their strikers and allowed to burn undisturbed until they self-extinguished. After burning ceased, the residue and remaining slag were collected; the slag was weighed in order to approximate the extent to which the flare had burned. To collect the emission residue, both the pan and the aluminum sheets were washed thoroughly with DDD water. The mass of wash water used was recorded. The washings and slag from each flare were placed in separate round-bottom flasks and stirred for ten minutes at 70-80^{o}C before being allowed to cool to room temperature. In order to permit the insoluble, non-perchlorate residue to settle, the flasks were placed in a refrigerator at 4^{o}C overnight. An aliquot was subsequently taken, filtered through a syringe, and placed in an LC vial to be analyzed.

Analytical Method. Perchlorate and nitrate analyses were performed on a Hewlett-Packard 1100 liquid chromatograph equipped with a photodiode array detector, with signal and reference wavelengths set as 280nm and 360nm, respectively. Separations were performed on a 250mm x

4.6mm Vydac 302IC4.6 anion column; the eluent was a 4mM solution of isophthalic acid buffered to an approximate pH of 4.9 using sodium tetraborate. A flow rate of 2 mL/min and injection volumes of both 10μL and 100μL were employed. Since the isophthalic acid buffer absorbed at 280nm and the perchlorate anion did not, analyte peaks were negative. Standard curves were prepared using a standard containing both perchlorate (100-1000 ppm for unburnt flares and 5-100 ppm for burnt residue) and nitrate (1000-10000 ppm). Residues from burnt Orion flares were sent to an outside laboratory for analysis using EPA Method 314.

3. Results

Analysis of aqueous rinses of the burn or detonation area resulted in large quantities of solution—up to 25L in the case of one emulsion explosive. Analysis yielded the parts-per-billion perchlorate present, and this was converted into total mass of perchlorate remaining. To make comparisons among the various devices studied, perchlorate remaining was reported both as percentage of original perchlorate and as milligrams (mg) remaining per gram (g) of energetic material (flare, propellant or explosive). It should be noted that for the explosives, the total perchlorate and nitrate were determined by extrapolation from actual percentage surface covered with foil (i.e. ten perchlorate spiked shots at 48% and three as-received shots at 64%) and actual or estimated percentage of foil recovered (i.e. ten perchlorate spiked shots at estimated 94% and three as-received shots ranging from 93% - 94%) to 100% coverage of the interior surface area of the detonation chamber and 100% foil recovery. For the propellants and the flares, an attempt was made to collect all the residual perchlorate. This was easier for the flares than for the propellant. The flares left large quantities of visible residue, and all the flares burned were small enough to fit in the catch pan. The propellant left almost no visible residue (occasionally if a paper wick was used in the initiation, it left char); furthermore, it was difficult to contain the residue from the large motors, which were burned outdoors.

3.1 Explosives:

Ten detonations of perchlorate-spiked emulsion explosives (six with MagnaFrac and four with Apex Elite) were analyzed for remaining perchlorate and most for remaining nitrate (see Table 1). For the ten detonations, the amount of perchlorate remaining after detonation, based on 48% coverage, was about 9%, of the initial perchlorate spike on average —regardless of the quantity of the spike or the nature of the emulsion explosive. Each of the ten detonations was extrapolated to 100% coverage and 100% recovery, and the average was about 21%. Three shots were performed with Magnum Ultra, which, according to Orica, contained 5.6% perchlorate. When this emulsion explosive was detonated, dramatically lower perchlorate levels were found: 0.035% of initial perchlorate (after extrapolation from 64% to 100% coverage and 93% - 94% recovery) and 0.019 milligrams perchlorate per gram of total charge. Apparently, the first set of tests involving hand-kneading NaP into the already blended emulsion explosive did not sufficiently blend the perchlorate into the explosive. Much of the perchlorate, instead of participating in the detonation, spalled off the original charge. The NaP added to formulations at the factory were homogeneously distributed and evidently the charge utilized the perchlorate more efficiently.

3.2 Propellant:

The presence or absence of aluminum did not appear to affect the efficiency of perchlorate consumption. Although there was concern that collection efficiency would be significantly decreased in the outdoor tests (B5, B6, B7), the amounts of perchlorate recovered from these shots do not appear lower than those from the small motors. In general, 0.0022% perchlorate remained compared to initial perchlorate or 0.014 on a milligram perchlorate to gram propellant basis (Table 4).

3.3 Flares:

Visual examination of the Orion and Chinese flares showed little difference. Both were housed in cardboard tubes with the ends rolled and plugged with a cardboard disk of several layers. The striker side was sealed by a hard black ignition tip much like that of a common kitchen match, but much larger. The outside of the U.S. flare had a texture similar to cardboard tubing from a roll of paper towels or wrapping paper. The Chinese flares were coated with a layer of wax, which gave their surfaces textures analogous to wax-coated drinking cups. The Orion flares contained light-colored sawdust interspersed throughout the filler. The Chinese flares had sawdust darker in color and filler oilier than the Orion flares. The ignition tips of all the flares were comprised of a hard, black material, probably containing magnesium, as suggested by lighting a small quantity. The ignition tips of the 5- and 10-minute Chinese flares were roughly the same volume as the Orion flare tips - cylinders ~3cm long by ~ 7mm in diameter. The 15-, 20-, and 30-minute Chinese flare tips were slightly larger (~4cm by 7mm), but the ignition tips of all the Chinese flares were lighter in color and more susceptible to crumbling than those of Orion.

The MSDS of the Orion flares indicated that the filler consisted of less than 10wt% $KClO_4$, ~75wt% $SrNO_3$, less than 10wt% sulfur and less than 10wt% sawdust/oil binder. To establish the uniformity of the perchlorate concentration throughout the flare, several flares were sectioned into three equal pieces, each of which was analyzed for perchlorate content. Results in Table 5 show there was little variation in nitrate or perchlorate content along the length of a flare. Extrapolating the data in Table 5, the total amount of perchlorate in each flare was estimated.

Although there is some flare-to-flare variation, on average all flares contained about 6wt% perchlorate, regardless of manufacturer, date of manufacture, or rated burn time. The flares were not completely consumed in the burn; slag representing about 50% of the original flare weight remained in all cases (Table 6). A sulfur-smelling compound could be dissolved from the slag by hot water. The insoluble portion of the slag had a basic pH; when treated with nitric acid, it formed a complex that produced a red color in a flame test.[9] These results plus the white appearance suggested the insoluble material was strontium hydroxide. The volume of slag was large and it was possible that perchlorate was trapped in the matrix and escaped combustion.

Perchlorate remaining after the flares burned varied dramatically. In general, more perchlorate, but not slag, remained from the Chinese flares than the Orion flares—at worse 1.5% of the original perchlorate. For the Orion flares, the remaining perchlorate was, at best, 0.005% of the original amount (Table 6). While this is a small amount of perchlorate, road flares are used quite widely,[10] and it is common for them to be extinguished and discarded before a complete burn. Thus, the role of road flares in perchlorate contamination of the environment could still be significant.

4. Discussion

In conclusion, Table 7 summarizes our findings for the efficiency of consumption of perchlorate in the functioning of various energetic devices—flares, propellants, explosives. It is acknowledged that our experimental techniques may allow trace amounts of perchlorate to escape detection. Therefore, the numbers reported represent the minimum amounts of perchlorate released. Nevertheless, some surprising trends are evident. The propellant is most efficient in consuming perchlorate—more efficient than emulsion explosives or flares. Discounting our hand-mixed explosives, flares are the least efficient in consuming perchlorate.

Table 7 shows our attempt to evaluate the extent to which these energetic devices cause perchlorate contamination in the environment. Although annual tonnage used appears in Table 7, all three entries required unsupported assumptions. The U.S. Geological Survey recorded the amount of explosives used in the U.S. in 2005 as 3.2 million metric tons (mmt) with 3.17mmt being ammonium nitrate (AN)-based explosives.[16] However, only a fraction of those explosives are packaged explosives, 100,000mt, and of those it is estimated only 5% contain perchlorate.[17] In Table 7 we use 8% of the packaged value to include any perchlorate introduced into the explosive by Chilean sodium nitrate.[4] [Only packaged products were considered because only they have the potential for other ingredients. The most extensively used AN explosive is ANFO made with only two ingredients—AN and fuel oil]. The estimate of 20 million pounds (~9000mt) of perchlorate for the DoD and NASA may be incorrect,[11] as the number of those devices used versus stored is not verified. That estimate may be an overestimate, perhaps as much as 50%. For road flares, the reported 40mt for one county in California was multiplied by 50 such counties; this number is undoubtedly an underestimate. When considering the overestimation of perchlorate from use in propellants and explosives and the underestimation of the contribution of flares, it appears that the contribution of road flares to environmental contamination by perchlorate may be significant. A more careful determination of the extent of perchlorate use in road flares and commercial explosives is required before the magnitude of this problem can be properly evaluated.

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Table 1: Ammonium Nitrate Emulsion Explosives

Explosive Pre-Blast Analys					Post-Blast Analysis						
	Shot	Total gram charge	Initial g ClO_4^-	initial % ClO_4^- in charge	% ClO_4^- residue/ initial ClO_4^-	mg ClO_4^- residue/ g charge	gram ClO_4^- residue	g NO_3^- recovered	initial g NO_3^-	% NO_3^- residue/ initial	mg NO_3^- residue/ g charge
as received MF		500									
MagnaFrac	1	472	18.09	3.83	**19.89%**	**7.61**	3.60	--	288		
69.43 wt% AN	2	495	21.69	4.38	**29.07%**	**12.74**	6.30	7-13mg/L	302	0.01%	**0.22**
9.91 wt% SN	3	492	20.14	4.10	**27.62%**	**11.32**	5.56	< 20mg/L	300		
Na lactate	4	516	38.74	7.51	**24.84%**	**18.65**	9.62	< 20mg/L	315		
water	5	505	38.18	7.56	**21.58%**	**16.32**	8.24	< 10mg/L	308	0.01%	**0.22**
	6	531	39.47	7.44	**13.80%**	**10.27**	5.45	--	324		
as received AE		500									
Apex Elite	7	477	18.19	3.81	**27.33%**	**10.42**	4.97	0.28	240	0.26%	**1.30**
56.83 wt% AN	8	496	18.93	3.82	**21.26%**	**8.12**	4.02	0.29	249	0.26%	**1.29**
8.61 wt% SN	9	528	40.53	7.67	**11.52%**	**8.84**	4.67	0.23	266	0.19%	**0.96**
Al added	10	533	39.31	7.38	**11.40%**	**8.41**	4.48	0.1	268	0.08%	**0.42**
Average					20.83%	11.27	5.69	0.23		0.13%	0.74
Std Dev					0.07	3.67				0.00117	
Magnum Ultra											
67.68 wt% AN	a	516	28.67	5.56	**0.022%**	**0.0121**	0.0037	0.039	288	0.023%	**0.13**
4.57 wt% SN	b	522	29.00	5.56	**0.043%**	**0.0241**	0.0076	0.094	291	0.053%	**0.30**
6.84 wt% NaP	c	520	28.89	5.56	**0.040%**	**0.0220**	0.0069	0.091	290	0.052%	**0.29**
Water ~9% Na lactate 0.25 + wax											
Average					0.035%	0.019	0.0061	0.0746		0.043%	0.24

* - The values for residual amounts, both perchlorate and nitrate, have been extrapolated to 100% room coverage and 100% foil recovery.

* - Shots 1 and 6 were not analyzed for nitrate content.

Table 2: Perchlorate Residue Removed from Aluminum Witness Material in Three Rinses

	Spiked Shots										As Received		
	MagnaFrac						Apex Elite				MagnaUltra		
	Shot #1	Shot #2	Shot #3	Shot #4	Shot #5	Shot #6	Shot #7	Shot #8	Shot #9	Shot #10	Shot #11	Shot #12	Shot #13
Rinse #1 (g)	0.54	2.31	1.98		3.16	1.39	1.65	1.45	1.63	1.09			
Rinse #2 (g)	0.63	0.44	0.45		0.44	0.94	0.28	0.31	0.42	0.77			
Rinse #3 (g)	0.08	0.1	0.08		0.12	0.13	0.32	0.06	0.06	0.16			
Total (g)	1.25	2.85	2.51	4.35	3.72	2.46	2.25	1.82	2.11	2.02	0.0022	0.0046	0.0041

* - The rinses for Shots #4, #11-#13 were all mixed together before having only one sample analyzed.

Table 3: Formulation of Propellants

		Organics								Solids			
ID		HTPB	CTPB	DOA	HX-878	IPDI	Formrez SUL-4	DER-331	Versamid 140	AP 300um	AP 90um	Al	Total Weight
burn A	g	4.00		0.50	0.14	0.37	3 drops			15.00	5.00	0.00	25.00
	%	16.00		2.00	0.54	1.47				59.99	20.00	0.00	
burn B	g	4.00		0.50	0.14	0.37	3 drops			18.46	7.11	0.00	30.57
	%	13.08		1.64	0.44	1.20				60.38	23.26	0.00	
burn C	g	4.00		0.50	0.14	0.37	3 drops			18.46	7.11	0.00	30.57
	%	13.08		1.64	0.44	1.20				60.38	23.26	0.00	
B1	g	18.00		2.25	0.60	1.65	2 drops			67.50	22.50	22.50	135.00
B2	%	13.33		1.67	0.44	1.22				50.00	16.67	16.67	
B3	g	18.04		2.25	0.59	1.66	6 drops			65.79	21.99	2.24	112.56
	%	16.03		2.00	0.52	1.47				58.45	19.54	1.99	
B4	g		20.25	10.50	1.50			3.75	1.50	73.04	24.64	15.00	150.18
	%		13.48	6.99	1.00			2.50	1.00	48.63	16.41	9.99	
B5	g	284.00		35.30	9.10	26.30	~25 drops			924.30	460.00	35.30	1774.30
	%	16.01		1.99	0.51	1.48				52.09	25.93	1.99	
B6	g	274.89		35.44	8.87	35.51	0.53			1024.00	395.00	0.00	1774.24
	%	15.49		2.00	0.50	2.00	0.03			57.71	22.26	0.00	
B7	g	274.90		35.56	9.37	35.85	0.97			1024.00	395.00	0.00	1775.65
	%	15.48		2.00	0.53	2.02	0.05			57.67	22.25	0.00	

Key to Table 3:

HTPB = hydroxyl-terminated polybutadiene; CTPB = carboxyl-terminated polybutadiene; AP = ammonium perchlorate; Al = aluminum; DOA = dioctyl adipate (plasticizer); HX-878 = Tepanol^{tm} (a binding agent); IPDI = isophorone diisocyanate (curing agent); Formrez SUL-4 dibutyltin dilaurate (curing agent); DER-331, an epoxy; Versamid 140, a polyamide resin (used as a catalyst for DER-331).

Table 4: Ammonium Perchlorate Propellant

	Burn Location	Amount Burnt (g)	Length (cm)	Diameter (cm)	L/D	Volume (cc)	g/cc	Initial ClO_4^- (g)	ppb (µg/L) ClO_4^-	H_2O (L)	ClO_4^- residue (mg)	residue % ClO_4^-	mg ClO_4^- residual per g propellant
burn A	lab	24.60	9.1	1.3	7.0	12	2.0	16.67	3100	0.100	0.310	0.00186%	0.0126
burn B	lab	23.60	10.0	1.6	6.3	20	1.2	15.99	965	0.100	0.0965	0.000603%	0.00409
burn C	lab	30.18	10.0	1.6	6.3	20	1.5	20.45	1780	0.250	0.445	0.00218%	0.0147
Sawdust	lab								0.142				
B1	lab	58.00	22.0	1.6	14	44	1.3	32.75	460	0.115	0.0528	0.000161%	0.000910
B2	lab	53.74	22.0	1.6	14	44	1.2	30.35	6100	0.100	0.611	0.00201%	0.0114
B3	lab	57.69	22.0	1.6	14	44	1.3	38.11	7300	0.116	0.843	0.00221%	0.0146
B4	lab	43.90	22.0	1.3	17	29	1.5	24.18	25500	0.101	2.58	0.0106%	0.0587
B5	outside	1691.51	23.7	7.7	3.1	1101	1.5	1117.80	401	5.827	2.34	0.000209%	0.00138
B6	outside	1669.50	24.0	7.7	3.1	1118	1.5	1130.97	4230	6.622	28.01	0.00248%	0.0168
B7	outside	1737.35	25.3	7.7	3.3	1178	1.5	1175.90	357	4.755	1.70	0.000144%	0.000977

Table 5: Unburnt Flares—Uniformity Check (Units are mg)

	Nitrate Analysis (mg)						**Perchlorate Analysis (mg)**					
	Flare Section			Average	Standard	% Std	Flare Section			Average	Standard	% Std
Flare Origin	First	Middle	Last	full flare	Deviation	Dev.	First	Middle	Last	full flare	Deviation	Dev.
Orion												
15 min	4525	5098	5098	4907	331	7	496	518	508.782	507	11	2
15 min	3973	4035	4192	4067	113	3	411	393	450	418	29	7
15 min	4280	3963	4099	4114	159	4	467	490	443	467	24	5
Avg in Section	4259	4365	4463				458	467	467			
Std. Dev.	277	636	552				43	65	36			
% Std. Dev.	7	15	12				9	14	8			
Chinese												
5 min	5297	4423	6841	5521	1225	22	562	398	614	524	113	21
5 min	4217	4155	4237	4203	43	1	383	370	390	381	10	3
10 min	6460	6480	7605	6848	655	10	577	564	691	611	70	11
10 min	4035	4033	4043	4037	5	0	359	368	358	361	5	1
15 min	7813	6681	4165	6220	1867	30	806	668	414	630	199	32
15 min	3980	4023	4009	4004	22	1	424	411	433	423	11	3
20 min	5173	4114	6888	5392	1400	26	590	415	693	566	140	25
30 min	5559	4766	6037	5454	642	12	537	458	552	515	50	10
Avg in Section	5317	4834	5478				530	456	518			
Std. Dev.	1323	1107	1520				144	106	137			
% Std. Dev.	25	23	28				27	23	26			

Table 6: Flare Analysis Before and After Burn

	Flare Pre-Burn Analysis			Post-Burn Analysis				
	Flare	Initial ClO_4^-		Slag Remaining		ClO_4^-		
	g	g	%	g	%	residue / initial	mg per g flare	mg per flare
Chinese								
5 min	67	3.9	5.9%					
5 min	67	3.5	5.3%					
10 min	119	6.4	5.4%	58	49%	1.5%	0.809	97
10 min	121	6.5	5.4%	61	51%	0.15%	0.079	10
10 min	120	6.5	5.4%	65	54%	0.18%	0.098	12
15 min	163	10.6	6.5%	83	51%	0.063%	0.041	7
15 min	160	10.4	6.5%	81	51%	0.073%	0.047	8
20 min	203	11.5	5.7%	103	51%	0.088%	0.050	10
20 min	202	11.5	5.7%	102	51%	0.10%	0.056	11
20 min	200	11.4	5.7%	101	50%	0.082%	0.047	9
20 min	201	11.5	5.7%	101	50%	0.055%	0.032	6
30 min	282	16.3	5.8%	141	50%	0.11%	0.062	17
30 min	281	16.3	5.8%	139	49%	0.13%	0.077	22
30 min	284	16.5	5.8%	142	50%	0.077%	0.045	13
Orion								
15 min	184	11.5	6.2%	94	51%	0.040%	0.025	5
15 min	176	11.0	6.2%	87	49%	0.005%	0.003	0.6
15 min	176	10.9	6.2%	88	50%	0.057%	0.035	6.2
15 min	174	10.8	6.2%	67	38%	0.005%	0.003	0.6
	Average					0.169%	0.094	15
	Standard Deviation					0.0036	0.1922	

Table 7: Summary of Perchlorate Residue & Estimated Annual Contamination

Average	% ClO_4^- remain/initial	mg ClO_4^- per g item	% NO_3^-		metric tons used annually	est. m tons with ClO_4^-	mg ClO_4^- residual	kg ClO_4^- residual
			remain/initial	of charge				
Flare	0.17%	0.094			2.00E+03	2.00E+03	1.88E+08	188
Propellant	0.0022%	0.014			1.13E+04	1.13E+04	1.59E+08	159
Hand-mix AN emulsion	20.8%	11.3	0.13%	0.74	1.00E+05	8.00E+03	1.52E+08	152
Commercial AN emulsion	0.035%	0.019	0.043%	0.24				