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## **Viability of Applying Curie Point Pyrolysis/Gas Chromatography Techniques for Characterization of Ammonium Perchlorate Based Propellents**

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# **Viability of Applying Curie Point Pyrolysis/Gas Chromatography Techniques for Characterization of Ammonium Perchlorate Based Propellants**

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## **Abstract**

Curie Point pyrolysis-gas chromatography was investigated for use as a tool for characterization of aged ammonium perchlorate based composite propellants <sup>(1)</sup>. Successful application of the technique will support the surveillance program for the Explosives Materials and Subsystems Department <sup>(1)</sup>. Propellant samples were prepared by separating the propellant into reacted (oxidated) and unreacted zones. The experimental design included the determination of system reliability followed by, reproducibility, sample preparation and analysis of pyrolysis products. Polystyrene was used to verify the reliability of the system and showed good reproducibility. Application of the technique showed high variation in the data. Modifications to sample preparation did not enhance the reproducibility. It was determined that the high concentration of ammonium perchlorate in the propellant matrix was compromising the repeatability of the analysis.

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## **Introduction**

Surface reactions due to aging of propellants can adversely affect the ignition and combustion characteristics of these deflagrating materials. Ultimately, burn rate or explosive sensitivity could yield out-of specification results rendering the propellant useless. The surveillance program utilizes many bulk methods such as thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) to evaluate and/or predict the performance of these propellants. However, these bulk techniques have difficulty addressing the potential chemical difference between propellant surface reacted zones (thin veneers) and the internal bulk material. Pyrolysis is a technique that accepts microgram sample sizes, and would complement existing bulk analysis. It would also complement the microscopic visual imaging techniques that currently exist, as a small sample from the visualized reacted zone would be enough for this pyrolysis technique. Together the data from these techniques could be used to predict propellant performance.

Pyrolysis is the characteristic breaking apart of large molecules into smaller ones using only thermal energy. This technique has been successfully applied to the analysis of macromolecules such as polymers and is routinely used to analyze complex substances such as tire rubber, textiles, dried paint, glue, paper coatings, petrochemical sources, plant materials, coal and bacteria<sup>(2)</sup>. Since most of these materials are primarily organic in nature, pyrolysis applications specific to these compounds are organic matrix analyses<sup>(3)</sup>.

The most critical elements of a pyrolysis unit are the uniformity and reproducibility of the temperature. These elements should yield the same thermal energy and therefore the same (reproducible) bond cleavage patterns for a given molecule or set of molecules. Reaching the pyrolysis temperature quickly is also important. This allows the thermally desorbed compounds and pyrolytically cleaved macromolecule fragments to be transferred to a gas chromatograph (GC) capillary column as a narrow band. To achieve this performance a curie point pyrolyzer was chosen<sup>(4)</sup>.

## **Experimental Design**

### ***Curie Point Pyrolyzer***

The Curie Point pyrolyzer uses a radiofrequency (RF) generator and a ferromagnetic foil. A ferromagnetic foil was inductively heated by a 225 watt 930 kHz RF coil to its curie point. The curie point is the point where the Pyrofoil loses its magnetic properties and energy is no longer absorbed so the temperature ceases to rise. The Temperature Raise Time (TRT) was only 0.2 sec and is reproducible. The resulting system reaches temperature quickly with reproducible analytical results. The system used was the Japan Analytical Instrumentation JHP-3 Curie Point Pyrolyzer.

The transfer tubing needle was installed into the GC column inlet with a heater surrounding it to avoid cold spots and potential cold trapping of hot pyrolyzate gases. The  $\mu$ grams of sample were wrapped in a pyrofoil and inserted in a quartz sample tube. The

sample tube was installed through the airlock valve without interrupting the carrier gas flow. The pyrolyzer was subsequently purged of air via the purge gas inlet and leak valve. This design allowed for rapid sample throughput without disrupting chromatographic conditions.

Pyrolysis temperature and initial sample size limits were established with recommendations from several literature sources. A temperature of 590°C and a sample size between 320 and 420 µg was chosen for this investigation.

The pyrolysis unit oven and transfer tubing heater was set at a temperature of 200°C to prevent cold trapping. A pyrolysis time of three seconds was considered to be the optimum pyrolysis time for the relatively low molecular weight organic compounds in the propellant. The organic content of the AP-based propellant was less than 0.25 %. The selected pyrolysis time ensured complete pyrolysis and thermal desorption. The helium flow through the pyrolyzer and into the GC inlet was set at 54 mL/min to affect a rapid sweep of the pyrolyzate gases onto the GC columns. The JHP-3 was mounted on the GC inlet. Figure 1 shows a diagram of the Curie Point pyrolyzer and gas flow through the system.

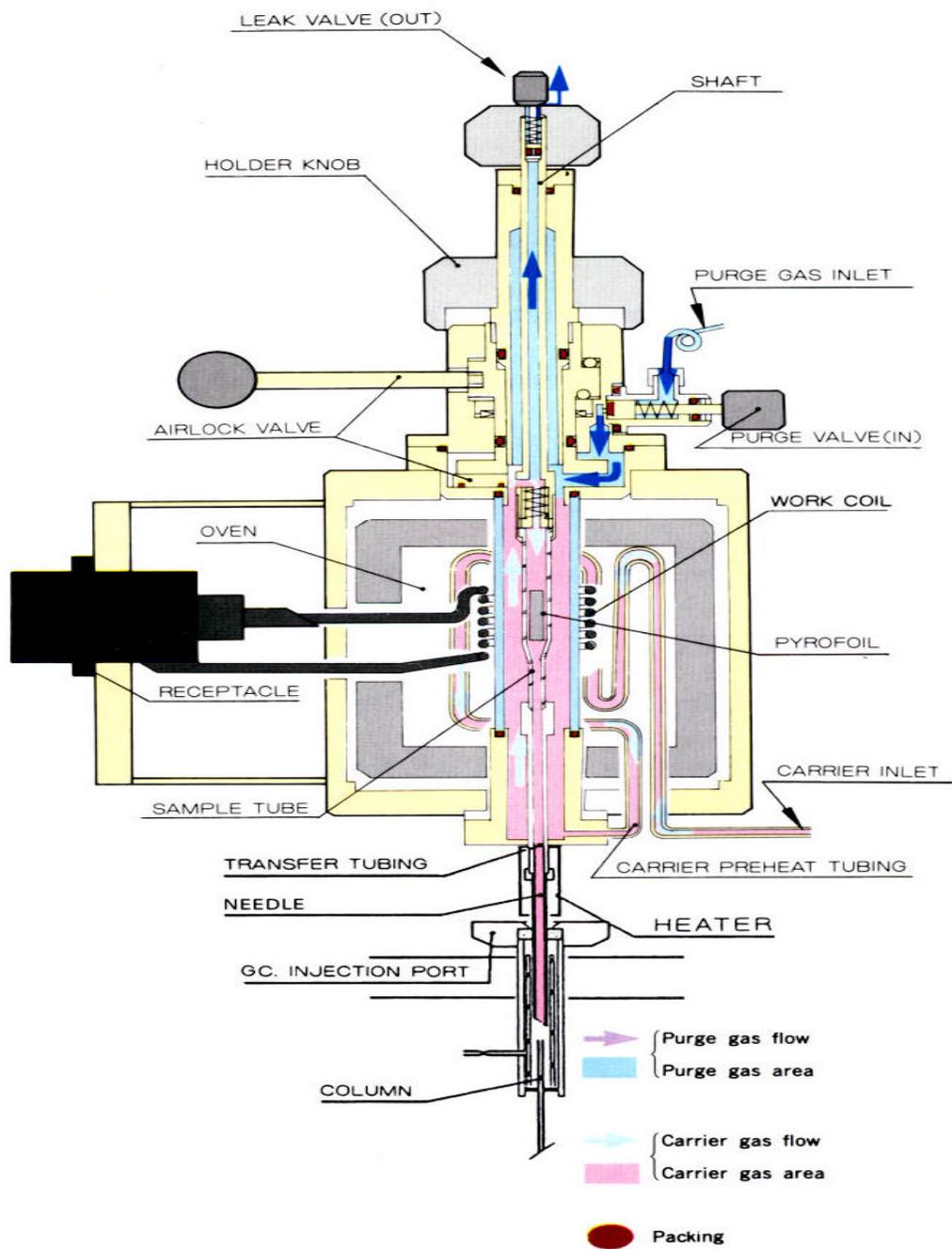


Figure 1: JHP-3 Curie Point Pyrolyzer

## *Gas Chromatograph*

The gas chromatography (GC) system utilized a three-column orientation with dual detectors and computer software for acquiring and integrating the two signals. The triple column assembly allowed the use of a vent column and two columns of different selectivity (polarity) providing the best separation for both polar and non-polar compounds<sup>(4)</sup>.

All analyses were performed using the following parameters:

- Analytical columns: consisted of two capillary columns in parallel both 30 m long x 0.32 mm I.D. a 0.25 $\mu$ m film thickness stationary phases. The stationary phases were DB-1 and DB-FFAP.
- The third column was the splitter or vent column and was 3 m long x .32 mm.
- Carrier gas flow was set at 2.0 mL/min/ analytical column and 50 ml/min for the vent column.
- The injector temperature was set at 225°C.
- Detectors were dual flame ionization detectors (FIDs).
- Detector makeup gas flow was 30 mL/min/ detector.
- Detector flame fuel gases were hydrogen flowing at 30mL/min/detector and air flowing at 300mL/min/detector;
- Detector temperature at 300°C.
- Detector sensitivity: 10<sup>-11</sup> Amperes Full Scale/mV.
- The column oven program: 50 ° C (2 minute hold) to 200 ° C at 10 ° C/min (10 min hold).
- Total analysis time 27 minutes.

Data acquisition was accomplished using a Dell Optiplex XMT 5100 with Varian Star Chromatography Workstation version 4.51. The analytical assembly is pictured in Figure 2.



**Figure 2: Assembled pyrolyzer, GC and data acquisition system.**

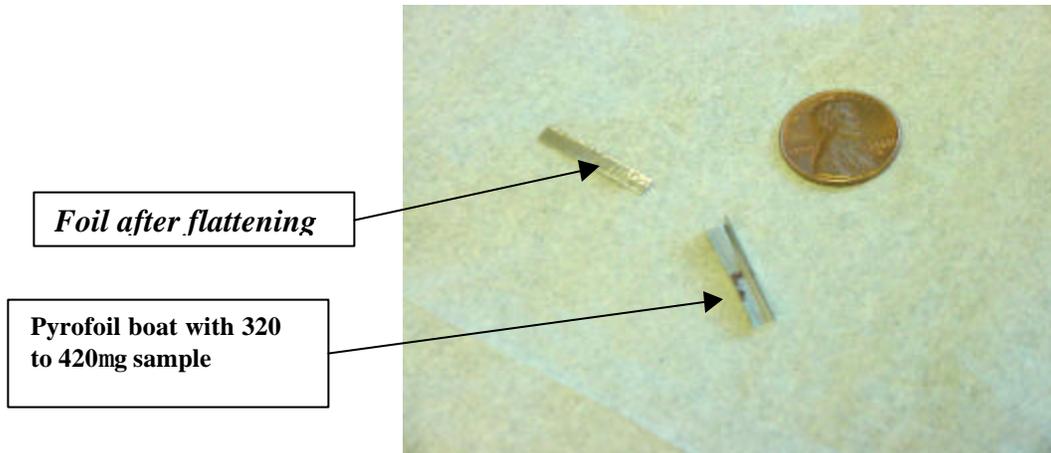
Pyrolysis data utilized in this study had to be acquired from the DB-1 column. The DB-FFAP column did not perform satisfactorily upon multiple pyrolyses of actual AP-based propellants. The DB-FFAP as mentioned previously is a high polarity column and will show high retention for polar compounds many of which are oxygenates. The pyrolysis of an oxidant created an oxidizing environment. This environment created many oxygen-containing compounds. Retention of these compounds on the DB-FFAP column ultimately led to active sites on this column and thus peak tailing. The DB-1 showed no preferential retention for these oxygenates and did not retain these compounds. Comparison of the data showed that the DB-1 was robust in this application and the DB-FFAP was not. This is evidence of adverse oxidation reactions occurring during pyrolysis of AP-based propellants.

### ***Sample Preparation***

A foil crimper was used to make a boat shape out of a 590°C Pyrofoil seen in Figure 3. Approximately 400 $\mu$ g of polystyrene molecular weight (MW) 2600 atomic mass units (amu) was weighed out and placed in the middle of the pyrofoil boat. The pyrofoil was then folded around the sample and then placed in the pyrofoil tube as shown in Figure 4. The flattened foil was placed in the quartz sample tube and was screwed on to the holder assembly. This assembly was then attached to the top of the airlock with an o-ring seal. Once the assembly was sealed, the purge gas valve was opened and helium was purged through the leak valve three times on one-minute intervals. This step was used to ensure that air and most importantly oxygen was purged from the system to avoid adverse oxidation reactions from taking place. With the sample holder purged, the airlock could then be opened and the quartz tube sample holder plunged into the pyrolyzer oven. The sample was given five minutes to come to temperature equilibrium within the oven. Then, pyrolysis was carried out for three seconds.



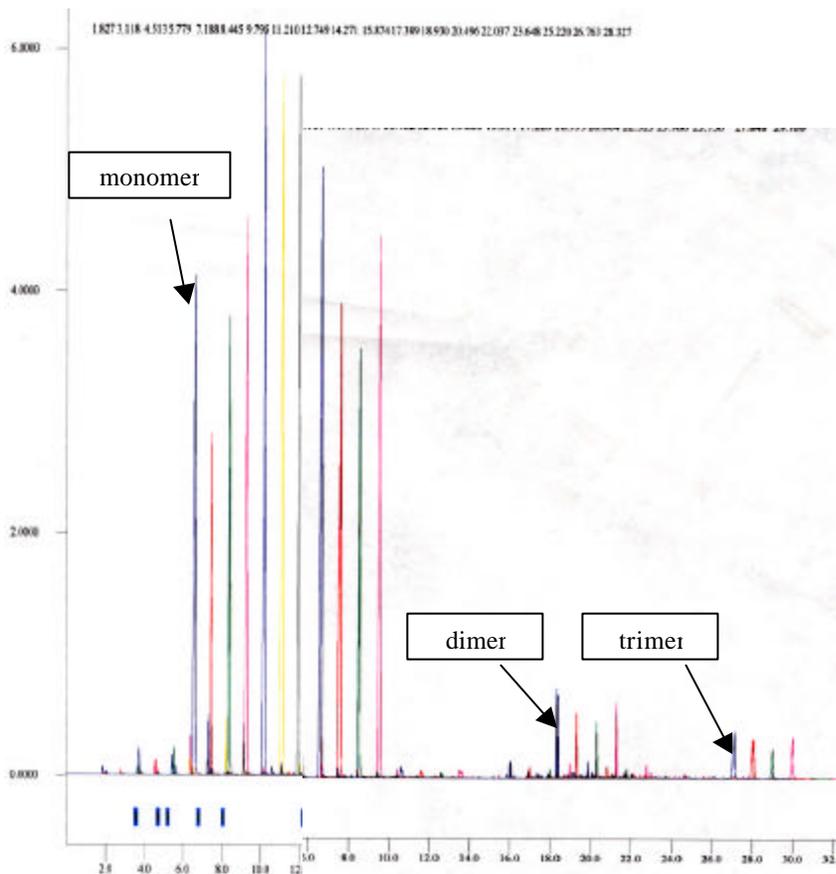
**Figure 3: Crimper and crimped pyrofoil boat.**



**Figure 4: Pyrofoil boat with sample and flattened pyrofoil.**

## System Reproducibility

The sample preparation and analysis was repeated for several replicates on the same polystyrene sample to investigate the reproducibility of the technique. Polystyrene is a commonly used calibration standard because of the reproducibility of three significant peaks per pyrogram consisting of the monomer, dimer and trimer of polystyrene (Figure 5). These three peaks plus several prominent peaks were chosen for area integration for comparison between the pyrogram replicates. Small sample size variances are apparent in the visible peak height differences on the staggered polystyrene pyrograms. Subsequently, the integrated area for each peak inclusive of the monomer, dimer, trimer and the several prominent peaks for every pyrogram was divided by the sum total area of all these peaks in the pyrogram and multiplied by 100 to yield the area percent of each peak. The average relative percent standard deviation was 3.747. Even with sample size differences on the order of two as reflected in the total areas the highest %RSD was approximately 16% with all others being less than 10%. The pyrolysis method was highly reproducible for this polystyrene matrix.



**Figure 5: Overlaid pyrograms of polystyrene Mw 2600. The monomer, dimer and trimer peaks are staggered with respect to the retention time axis due to staggering of the overlays.**

An additional presentation of the pyrolysis data of polystyrene is shown in error bar form in Figure 6. This presentation was made to show the high degree of reproducibility the polystyrene Mw 2600 amu pyrolysis achieved. Again, the method appears to have great potential.

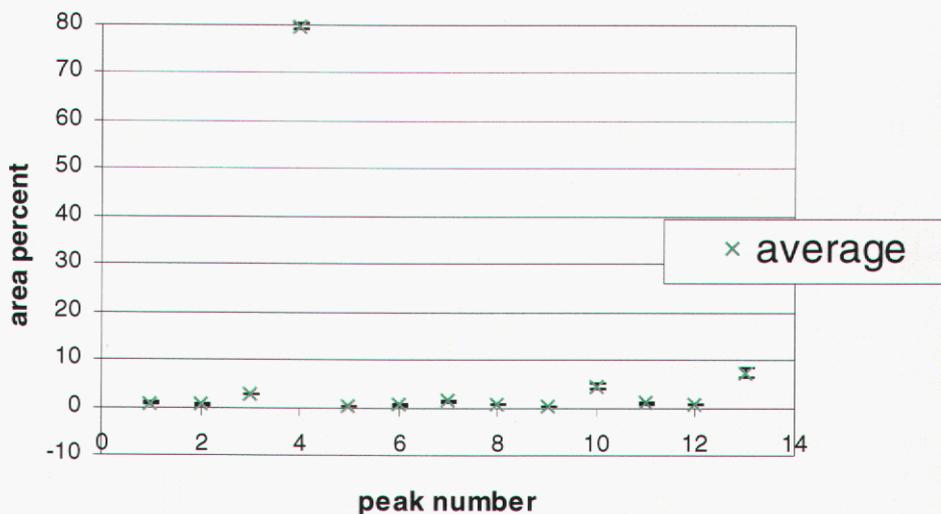


Figure 6: Peak number vs area percent mean +/- 99% confidence interval polystyrene Mw 2600 showing reproducibility of polystyrene.

In Figure 6, peak numbers replaced retention times in ascending order, i.e. the earliest retention time was peak number 1 and the latest retention time was peak number 13. The variances were generally very small about the average area % showing good reproducibility between pyrolyses of the polystyrene Mw 2600 amu.

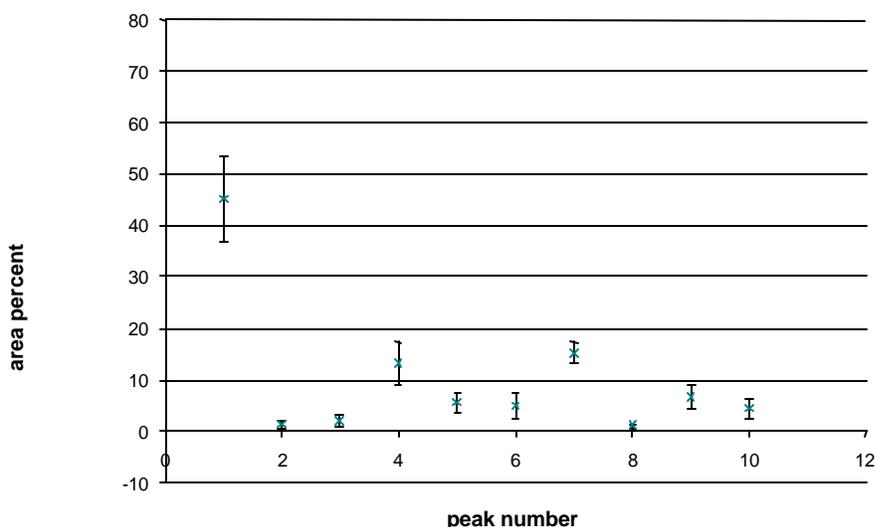
#### *Sample preparation and pyrolysis of Ammonium Perchlorate based propellants*

Once system reliability and reproducibility were established, pyrolysis of AP-based propellants was initiated. The 300-400  $\mu\text{gm}$  shaving of propellant was then placed in a pyrofoil and folded using a needle nose plier crimping technique. The pyrolyzer was purged of air and the sample allowed to equilibrate at the pyrolyzer oven temperature as previously described. Pyrolysis was performed as per conditions expressed above.

The first AP-based propellant samples analyzed were the unreacted zone of SN1035-I6, a 34 year old propellant. Again prominent and characteristic peaks for the six successive runs of this sample were chosen to evaluate the achievable reproducibility

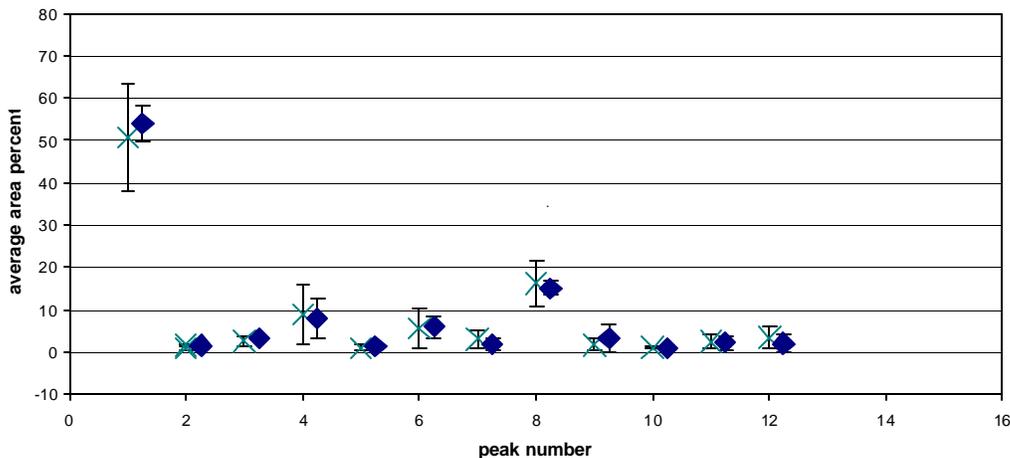
from the DB-1 column signal. Ten such peaks were used for the statistical breakdown of the area% data into average area %, standard deviation, variance and %RSD shown in Figure 6. Examination of the statistics shows much poorer reproducibility for the successive propellant analyses versus the polystyrene analyses. Only one %RSD was below 10% and over half the %RSDs were over 20%.

Area percent with +/- 99% confidence interval (variance) error bar presentation of AP-based propellant pyrolysis data was calculated. Peak numbers replace retention times in ascending order, i.e. the earliest retention time was peak number 1 and the latest retention time was peak number 10. The variances are generally a large percentage of the average area % showing poor reproducibility between pyrolyses of the unreacted SN1035-I6, 34-year-old propellant.



**Figure 7: Peak number vs. area percent mean +/- 99% confidence interval unreacted zone 34 year old propellant.**

The second AP-based propellant samples analyzed were both the reacted and unreacted zones of SN74C79, a 21 year old propellant. The reacted zone of this propellant was more darkly colored and more brittle than the unreacted zone and it was hoped that a marked difference in the pyrolysis signature of the two zones would be observed. Five replicates each of both zones were run and characteristic peaks were chosen for data reduction that was performed as in Figure 7 for the SN1035-I6 propellant. It was immediately observed that the prominent characteristic peaks for both the unreacted and reacted zones were identical. No new peaks appeared or pre-existing peaks disappeared between the two zones. The overlay of the two data sets with error bars in Figure 8 further demonstrates that no real differences can be discerned between the two zones by pyrolysis signature.



**Figure 8: Peak number vs average area percent +/-99% confidence interval unreacted zone vs reacted zone.**

Unloaded 590°C pyrofoils were folded, crimped and pyrolyzed as system blanks to verify that these blank pyrofoils were not contributing background to the AP-based propellant characteristic peaks and thus perturbing the reproducibility. A standard pyrofoil blank run was performed after conditioning the column. The quartz tube was propane cleaned. This process was initiated promoting a method change where the quartz tube was propane flame cleaned daily before pyrolysis. The column was always conditioned before pyrolysis with the exception of the worst-case blank pyrofoil experiment. The blank pyrofoils were not found to significantly contribute to the pyrogram background in the area of interest and were dismissed as a factor causing the irreproducibility.

Since even the worst-case blank pyrofoil contribution was insignificant, this high degree of irreproducibility was attributed to the complexity of the matrix, which was predominately inorganic ammonium perchlorate. However, attempts were made at pyrolyzing the reacted zone of the same propellant in hopes that significant changes would be observed. If only changes in peak area percents were observed, then these would have to exceed the error bar variances to be deemed “real” changes. Six replicates of the reacted zone of SN-1035-I6 were then pyrolyzed. The data was then examined for new or missing peaks or real changes in the area percentages of existing peaks.

The large error bars indicative of pyrolysis irreproducibility were inhibiting the ability to make distinctions between the zones of the two ages of propellants already addressed. Due to the sample matrix complexity perhaps the trivial sample preparation of shaving off chunks of propellant was inadequate to achieve a homogenous sample.

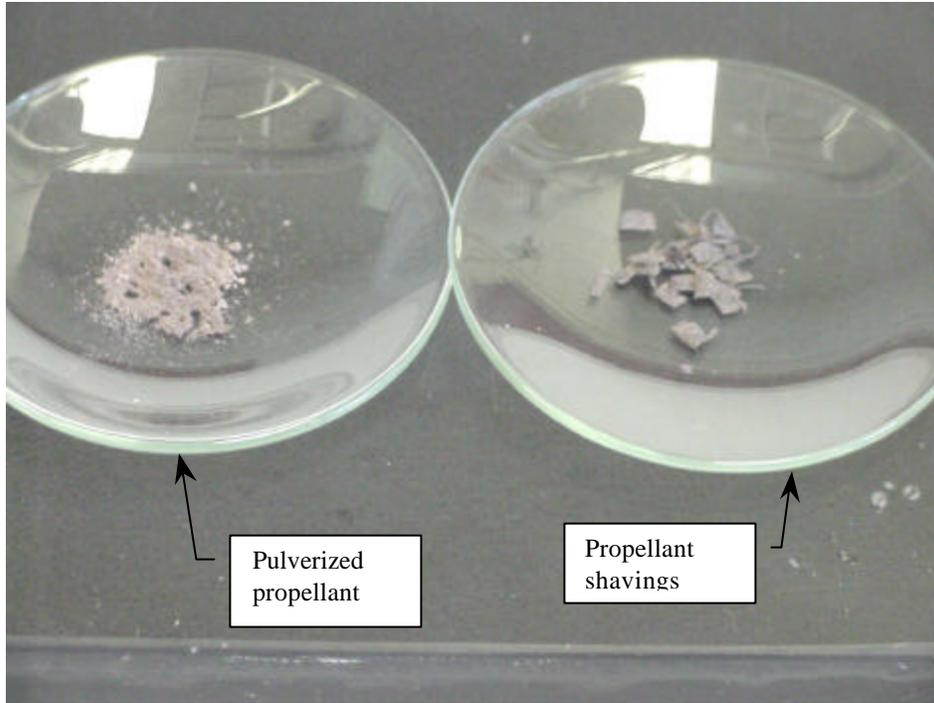
### ***Sample preparation of AP-based propellants***

Due to the sample matrix complexity a cryogenic crushing preparation technique was adopted<sup>(3)</sup>. The propellant is chilled in liquid nitrogen below its glass transition point and ball-milled to a fine powder. The cryogenic crusher to perform this task was unavailable at the time so a modified version was used.

A standard ball mill accepting stainless steel cylinders (sample holders) of approximate dimensions of 3cm long by 1cm in diameter enclosing a stainless steel (SS) ball and sealed with an end cap were utilized as seen in figure 8. The propellant shavings in the hundreds of milligram mass range was transferred to one of these cylinders with the SS ball inserted and the end cap attached. This whole assembly was lowered into a dewar of liquid nitrogen for a period of 5 minutes to chill the contents below the glass transition point of the propellant. The SS cylinder was inserted into the manifold and agitated for 5 minutes. This process was then repeated three more times to achieve the pulverized, finely divided condition of the propellant. The propellant before and after pulverization is shown in Figure 9.

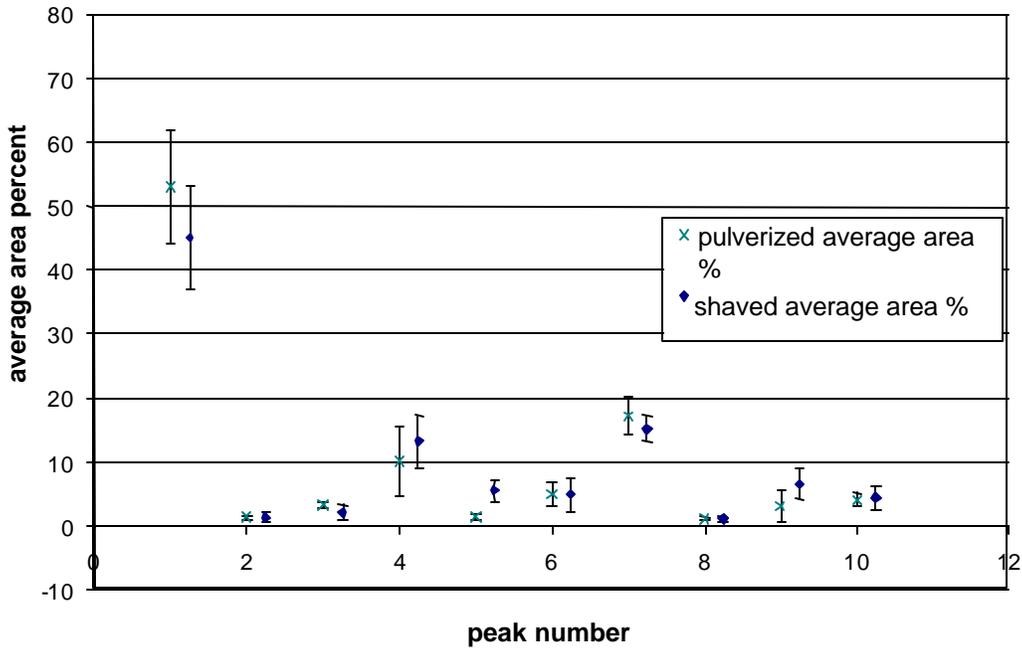


**Figure 9: Sample holder, end cap and SS ball bearing . This assembly is liquid nitrogen chilled prior to inserting in SS manifold for ball mill agitation.**



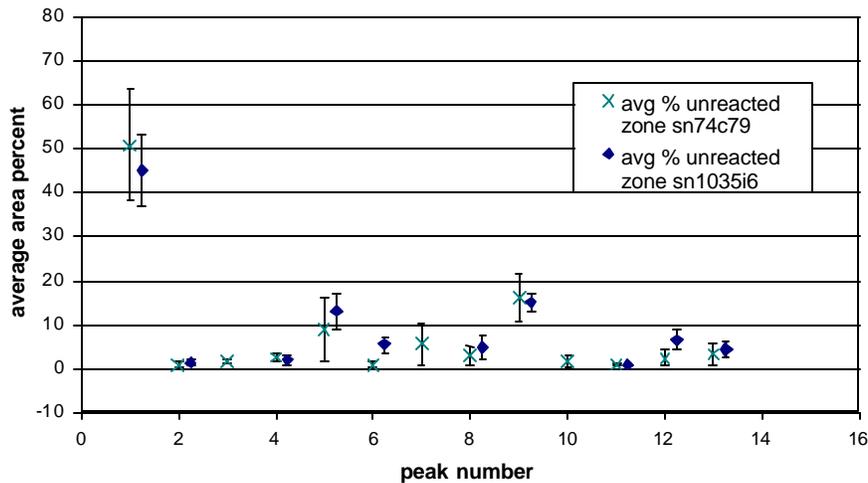
**Figure 10: Pulverized condition of the propellant shavings after the ball-mill process**

Five replicates of the pulverized version of SN-1035-I6 were performed and the data was manipulated to generate the average area % and 99% confidence interval error bars. Comparison of this data to the shavings data for the same propellant showed no significant improvement in reproducibility as seen in Figure 10. Since the same degree of reproducibility was achieved with or without pulverizing the propellant, the chances of achieving a homogenous sample with a high degree of reproducibility appeared more remote.



**Figure 11: Comparison of the pyrogram statistics of pulverized SN-1035-I6 to shavings of the same material. No improvement is noted.**

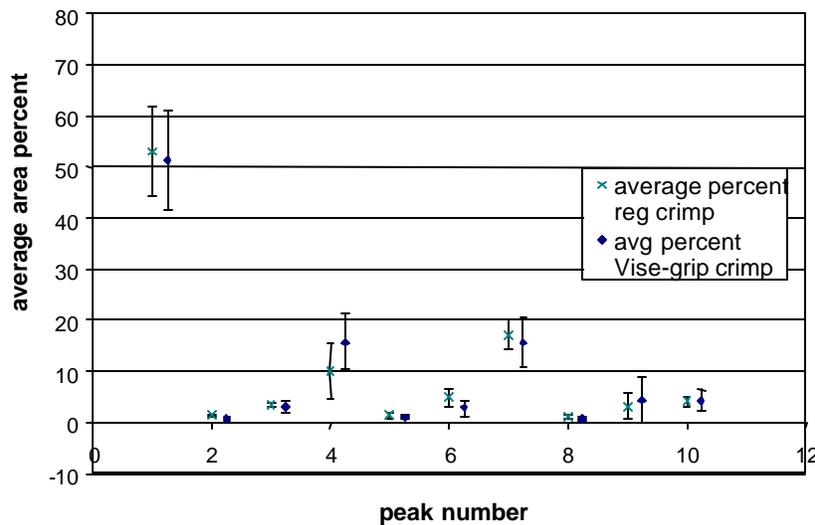
The older samples exhibited less homogeneity. The unreacted and reacted zones of 21 year old propellant SN74C79 had previously demonstrated more overlap in the average area % than the same zones of the older SN-1035-I6 propellant. This had been assumed to be due to less aging and, therefore, less chemical dissimilarity. Consequently, comparing the older SN-1035-I6 propellant reacted and unreacted zones to the younger SN74C79 propellant reacted and unreacted zones respectively should demonstrate less error for the younger (21 year old) SN74C79 propellant versus the older (34 year old) SN-1035-I6 propellant (Figure 12). The data does not reinforce this interpretation as the error was not consistently less for the younger propellant versus the older. In addition, the error was so significant as to prohibit distinguishing between the two ages of a given zone on the whole. Additionally, the appearance of peaks in the reacted or unreacted zone of a particular age, which may have been absent in the other age, are either too diminutive or too irreproducible to rely on as characteristic peaks for differentiation. The method remains too variable to correlate younger age to better overlap and less error.



**Figure 12: Comparison of the unreacted zones of the two different ages of the AP-based propellant. Tighter error bars for the younger propellant were not universally observed.**

In order for pyrolysis to succeed for this application a more reproducible pyrogram from replicate to replicate had to be achieved. Since finely dividing the sample matrix had not helped and age and irreproducibility could not be directly correlated, other aspects affecting the pyrolysis would need to be investigated.

For the above reason a different pyrofoil crimping technique was evaluated. This involved the use of a modified vise-grip that could have the closure pressure preset by an adjustable bolt on the handle<sup>(4)</sup>. The vise-grip was used to eliminate the non-uniform needle nose pliers crimping that had formerly been employed. The modified vise-grip also left a cylindrical conduit along one edge of the flattened pyrofoil that was to facilitate the movement of pyrolysate gases from the foil. This would minimize additional inter-reactions and would improve reproducibility. Five replicates of pulverized SN-1035-I6 prepared with the new technique were compared to the 5 run by needle nose plier crimping and no significant improvement was observed (Figure 13). Thus, the pyrofoil crimping technique was removed from consideration as a factor in the reproducibility problem.

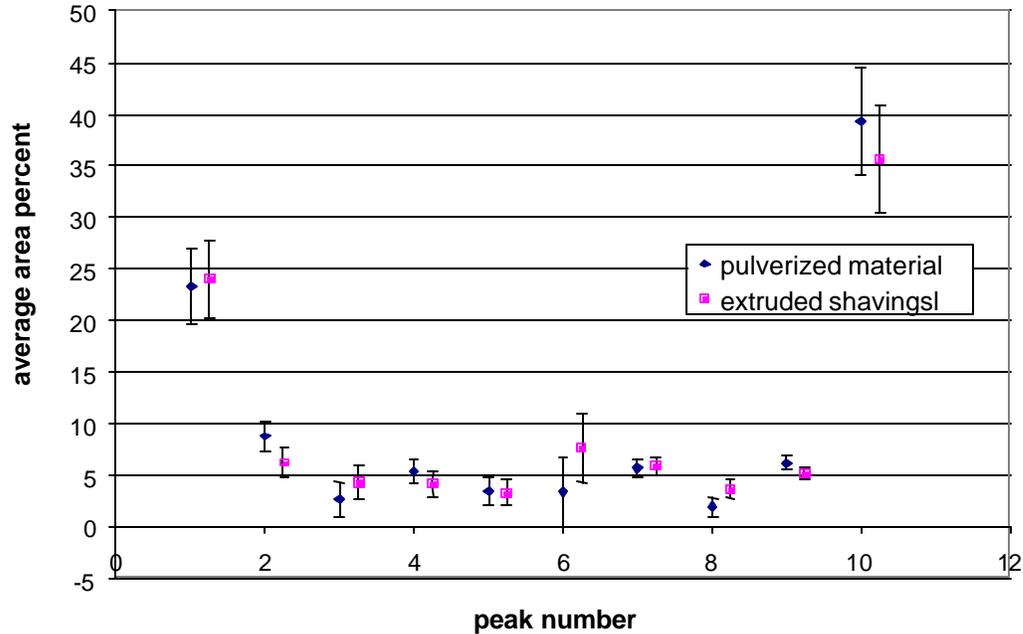


**Figure 13: The modified vise-grip technique did not improve the reproducibility of the technique as the error bars indicate.**

The hypothesis that the pyrolysis data was of a random nature because the sample aging process had created a heterogeneous matrix was then investigated. None of the propellants tested to this point were new unaged baseline materials.

A baseline factory fresh sample of AP based propellant was needed for pyrolysis testing. Hipel 430 TU47548 was used for this purpose. This material was immediately subjected to the more rigorous sample preparation of cooling and subsequent ball milling with a notable difference between the Hipel and the aged propellants. The aged propellants were initially harder materials, probably due to cross-linking associated with aging, and therefore, close enough to their glass transition point to crunch to a fine powder using this technique. The Hipel, on the other hand, was much more pliable and this technique did little more than cause the material to extrude as a sheet. The smallest pieces of this material had sample weights between 30 to 60  $\mu\text{gms}$  and these were subjected to pyrolysis analysis. Since no difference in reproducibility was observed between the trivial needle-nosed pliers flattening of the foil and the vise-grip technique all these foils were flattened with the needle nosed pliers. Again, some of the characteristic pyrolysis peaks for this

propellant exhibited %RSD's for replicates of greater than 20% as shown in Figure 14. The freshest AP-based propellant sample available still demonstrated large statistical variation all but eliminating sample age as the primary source of the irreproducibility.



**Figure 14: Average area% and 99% confidence interval error bars for the pyrolysis of both the pulverized and shavings of Hipel propellant. Both yield similar average area % distributions.**

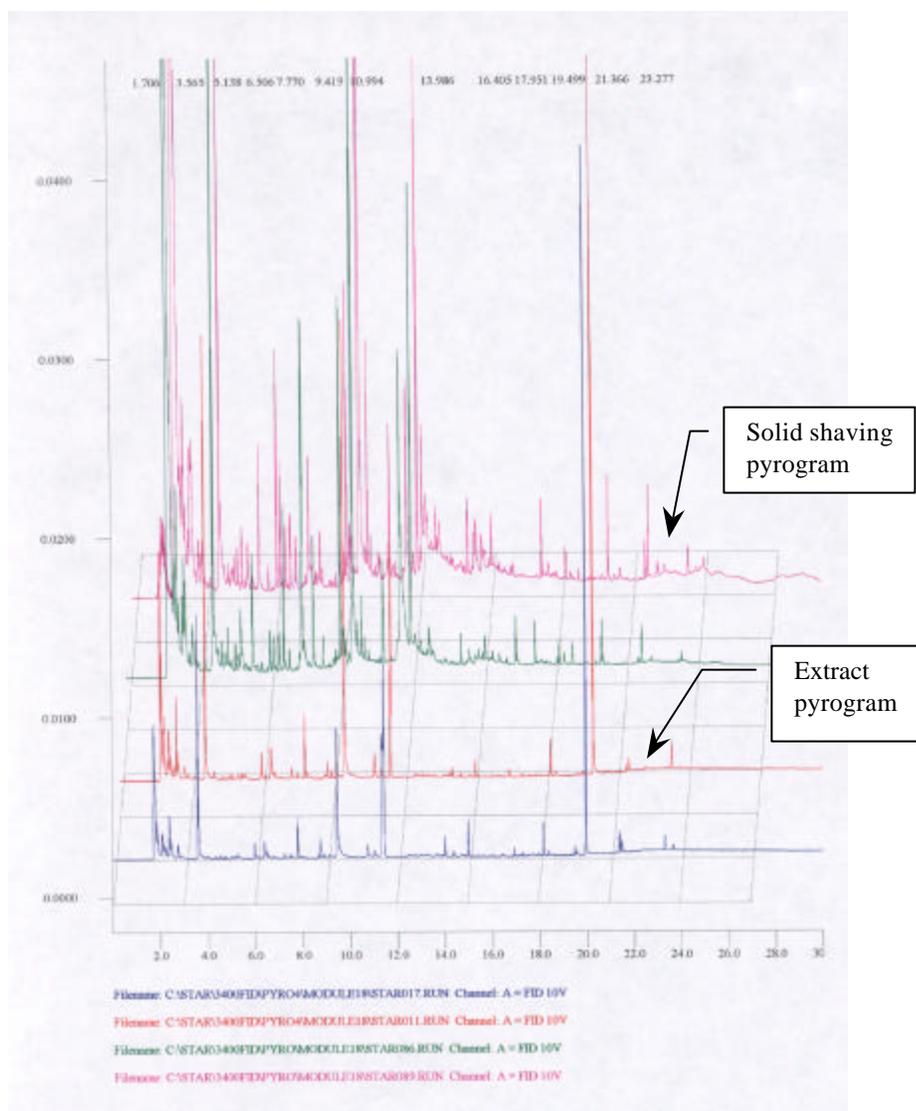
Even though the crushed versus shaved state of the older propellant material had presented no statistical advantage, a demonstrator model of a cryogenic crusher from Dychrome was applied to the Hipel propellant to finely divide this material and verify that aging effects were not factors in the pyrolysis irreproducibility. The cryogenic crusher utilized virtually the same stainless steel cylindrical sample holder, SS ball and endcap as previously described. The advantage presented by this device was the ability to agitate the sample while it was being chilled in liquid nitrogen. After 15 minutes of cryogenic crushing the resulting Hipel propellant was a finely divided material as thoroughly homogenized as possible.

However, as with the older propellant, the pulverized version of the Hipel still pyrolyzed with marked variability in the first 3 replicates attempted. No difference between shavings or pulverized material could be determined and, in general, no differences in ages or zones of propellants of similar formulation could be discerned.

### *Open foil pyrolysis of AP-based propellants*

A relatively simple experiment was designed to verify the reproducibility of open foil pyrolysis. Solvated compounds can be easily applied to a wire by dipping the wire in the solvent. Once the pyrofoil is folded into the boat configuration a small depression in the middle of the boat allows for the introduction of a liquid sample from a syringe. One hundred mg of AP-based propellants underwent extraction in 10 mL of tetrahydrofuran (THF) and were subsequently filtered with a 0.45  $\mu\text{m}$  Teflon filter to remove undissolved materials or flocculants. Those THF soluble components of the AP-based propellant were now evenly dispersed in the solvent and an aliquot of 10  $\mu\text{L}$  was carefully added to the pyrofoil boat drop by drop. Adding the sample drop by drop ensured quicker evaporation of the solvent to prevent wetting the entire foil and possibly losing some material. Again it must be reiterated that this test was designed to evaluate the efficacy of open foil pyrolysis and not to be considered method development for differentiation of ages of AP-based propellants. Basically, the solvation process would discriminate the sample on the basis of solubility and possibly disrupt existent cross-linking. These processes could easily mask the subtle changes being sought in the aging of AP-based propellants. However, if the pyrolysis of these solvent applied compounds in an open foil was reproducible then further investigation into applying the solid phase to the wire would be warranted.

The pyrolysis of THF solvent extractions of both unreacted and reacted zones of AP-based propellant SN-1045-I6 (34 years old) was attempted with open foil technique. Prior to pyrolyzing the extracts, blank THF was pyrolyzed to determine if the solvent residue would contribute peaks to the pyrogram. Only diminutive peaks were observed and these were excluded from consideration in deriving the characteristic peaks in the pyrograms. The solvent extraction did, as was expected, alter the relative abundance of some characteristic peaks and “cleaned up” the pyrograms seen in Figure 14. The loss of much of the peak definition and the change in relative abundance of characteristic peaks is primarily due to solubility limitations of these various components in THF. Although not representative of the bulk material, this solution of the THF soluble components should be a fairly homogenous sample resulting in reproducible pyrograms.



**Figure 15: Open pyrofoil pyrolyses of THF extracts.**

Unfortunately, pyrolysis of 5 replicates of the THF extracts of unreacted SN-1035-I6 still demonstrated high variation. For simplicity and due to the “clean” pyrogram, only 4 characteristic peaks were evaluated. Of these 4 peaks all of the %RSDs were over 15% and two were over 20%. The open foil pyrolysis technique had not improved the repeatability of the pyrolyses.

The irreproducibility could be either attributed to the matrix or the open foil pyrolysis technique. The matrix, even though solubilized in THF would retain some equilibrium amounts of inorganics, primarily ammonium perchlorate, a strong oxidizer, that could adversely affect the pyrolysis. The open foil pyrolysis technique could have inherent reproducibility problems. Unlike the crimped foil which guarantees intimate contact of sample surfaces to the ferromagnetic foil and, therefore, better heat transfer,

the open foil would heat the surface in contact with it first. If the thermal conductivity of the sample lagged to far behind the pyrolysis processes of fragmentation and thermal desorption, then pyrolyzate gases could sputter material from the foil surface resulting in irreproducible replicates. For this reason a test of the reproducibility of the open foil pyrolysis method was devised much like the crimped foil method had been verified with polystyrene

Ideally, a solvent mixture of the organic constituents of the AP-based propellant would be used to load the pyrofoil for open foil pyrolysis and this was attempted. The TP90B butyl carbitol formal plasticizer, the LP33 polysulfide monomer, p-quinone dioxime and the 1,3-diphenylguanidine were added at 20.6, 12.9, 6.1 and 3.2 mgs respectively to 100 mL of THF in a volumetric flask. The p-quinone dioxime white solid and the oily liquid polysulfide monomer were sparingly soluble in the THF and complete solvation did not occur. The THF solution did discolor slightly yellow due to the polysulfide monomer but round immiscible droplets of the monomer remained at the bottom of the flask. The p-quinone dioxime had been added in excess to attain maximum dissolution of this component and, therefore the equilibrium white solid remained at the bottom of the flask as well. This reinforced the notion that THF extracts of the propellant would discriminate on the basis of solubility. The resultant supernatant was filtered as in the AP-based propellant extracts and 3 replicates were subjected to open foil pyrolysis.

Ten peaks were chosen as characteristic peaks and 2 of the 10 had %RSDs above 20%. Two other peaks had %RSDs between 10 and 20% and the others were less than 10% as shown in Table 1. These results were significantly better than the THF extracts of the actual AP-based propellant, but some variability remained. At this point it was unclear as to whether changes from replicate to replicate due to solubility limitations manifested itself in higher % RSDs in some of the characteristic peaks or just reproducibility issues in open foil pyrolysis in general produced these variable results. One additional test was required to remove the solubility issue from consideration and evaluate open foil pyrolysis.

**Table 1: Open foil pyrolysis of organic ingredients of AP-based propellant in THF extract.**

Propellant ingredients in THF 3/20/2000							
	#1	#2	#3				
Retention Time	Area %	Area %	Area %	Avg. Area %	Std. Dev.	variance	% RSD
1.735	17.00	17.60	19.00	17.87	1.03	2.92	5.75
2.404	4.29	4.58	4.23	4.37	0.19	0.53	4.27
3.605	3.14	2.60	3.37	3.04	0.40	1.12	13.02
5.99	2.97	2.47	2.72	2.72	0.25	0.71	9.13
6.157	14.86	14.13	15.71	14.90	0.79	2.25	5.31
6.533	0.25	0.27	0.47	0.33	0.12	0.34	36.35
7.803	0.98	0.93	0.83	0.91	0.08	0.22	8.31
11.437	1.46	1.97	0.86	1.43	0.55	1.57	38.56
16.423	1.30	1.20	0.96	1.16	0.18	0.50	15.27
19.992	53.74	54.25	51.85	53.28	1.26	3.59	2.37

The test was performed on a three component system freely soluble in the solvent with no inorganic nature to it. The three components were dibutyl phthalate, diethyl phthalate and trimethylolpropane trimethacrylate. These were three conveniently available compounds and were easily solvated in isopropyl alcohol (IPA). As with the THF, blank IPA was pyrolyzed to exclude any IPA solvent residue peaks from being considered characteristic of the 3 component system. Table 2 shows that 5 replicates of open foil pyrolysis of these compounds demonstrated remarkable precision. All %RSDs were less than 5%. Consequently, the open foil pyrolysis appeared to be a reproducible technique in a matrix known to be free of inorganic and potentially oxidizing constituents.

**Table 2: Excellent precision was achieved with open foil pyrolysis of these soluble components in IPA.**

Phthalates and trimethacrylate in IPA 4/02/2000 pyrolysis by open foil									
	#1	#2	#3	#4	#5				
Retention Time	Area %	Avg. Area %	Std. Dev.	variance	% RSD				
14.363	29.35	28.20	28.20	29.13	28.26	28.63	0.56	0.86	1.96
18.159	53.28	53.27	53.08	52.06	52.69	52.88	0.52	0.79	0.98
18.836	17.37	18.53	18.72	18.82	19.05	18.50	0.66	1.01	3.55

Solvent extracts of soluble organic materials could be subjected to open foil pyrolysis with good reproducibility. THF extraction of the organic ingredients of the AP-based propellant demonstrated far better reproducibility than the THF extracts of the propellant itself. Again, in dealing with the propellant matrix itself reproducibility problems arise. Even though open foil pyrolysis appeared precise, application of the solid AP-based propellant to a curie wire was abandoned as nonviable. In every case

where system reliability had been proven with an amenable organic material the AP-based propellant matrix yielded poor precision.

The element common to all the repeatability problems was the AP-based propellant matrix or more specifically the inorganic content thereof. Even with the THF organic solvent extracts of the AP-based propellants some equilibrium ammonium perchlorate and other inorganic modifiers would be present. One last approach to the isolation of the AP-based propellant organics from the inorganics was attempted.

Ion chromatography is used to measure ammonium ion from the dissolution of AP-based propellant in distilled water (DI) water. The dissolution is accomplished by ball-milling chunks of propellant in a large excess of DI water in the same apparatus that cryogenic crushing of the propellant was achieved. The method yields quantitative extraction of ammonium ion from the sample and it was postulated that the remaining undissolved material might be primarily organic AP-based propellant constituents.

***Sample preparation isolating solid organics from inorganics in AP-based propellants***

Using the sample preparation technique for the dissolution of ammonium ion from AP-based propellants, attempts were made to quantitatively collect the remaining solid material. Two-hundred mg of SN1035-I6 and SN74C79 both unreacted and reacted zones were placed in 4 mL SS mixer mill vials with SS balls and end caps and mixed for 10 minutes. The aqueous liquids were carefully removed from the vials to leave the solid material undisturbed. The first extracts were observed to be rusty yellow in color. The extractions were repeated 3 more times with the second washes being rusty yellow, the third washes being light pink and the fourth washes being light pink to purple. After the last wash the water was decanted off and the SS mixer ball removed to allow the remaining solid material to dry. It was noted that a minute unknown quantity of solid material was irretrievably lost during the water removal processes affecting the percent weight loss data in Table 3.

**Table 3: Weights of AP-based propellants before and after extraction with DI water. % lost does not account for all the inorganic material including the ammonium perchlorate.**

		<b>Before Wash</b>	<b>After Wash</b>	<b>% Lost</b>
<b>SN1035-I6 Unreacted</b>		0.20081g	0.14541g	53.1
<b>SN1035-I6 Reacted</b>		0.20036g	0.05465g	72.7
<b>SN74-C79 Unreacted</b>		0.20032g	0.09408g	27.4
<b>SN74-C79 Reacted</b>		0.20079g	0.09987g	50.3

Since the AP-based propellant is approximately 74% by weight ammonium perchlorate losses of this magnitude were expected. However, only the SN-1035-I6 reacted propellant approached this figure and some of that loss included minute pieces lost in the decanting process. Although this extraction process was efficient for the removal of the bulk constituent ammonium perchlorate and subsequent ammonium ion determination by ion chromatography (IC) it was next to impossible to ascertain the remaining ammonium perchlorate or other inorganics in the residue. The red iron oxide (Fe<sub>2</sub>O<sub>3</sub>) burning accelerator and the magnesium oxide (MgO) burning suppressor, present at 2 and 1 percent respectively in the AP-based propellant, are insoluble to slightly soluble in water and would be left in the residue. In other words, even if all the ammonium perchlorate were removed from the organics some inorganic oxides would remain. Consequently, the pyrolysis of the residues of the unreacted and reacted zones of SN74C79 was highly variable. Washing the propellant with DI was not an effective way of removing the inorganic matrix and did not improve the pyrolysis reproducibility. High variability still exists with water extraction of AP.

**Table 4: Weights of AP-based propellants before and after extraction with DI water.**

SN74-C79 Reacted						
Retention Time	% Area	% Area	% Area	Avg. % Area	Std.Dev.	% RSD
3.031	12.06	10.41	11.80	11.42	0.89	7.78
3.627	25.04	44.60	35.79	35.14	9.80	27.88
6.102	18.39	14.07	15.74	16.07	2.18	13.55
7.829	7.03	12.84	9.77	9.88	2.91	29.45
10.852	9.81	3.58	6.59	6.66	3.11	46.72
11.531	26.28	13.65	18.97	19.64	6.34	32.30
14.211	1.39	0.84	1.34	1.19	0.31	25.68

## Conclusions

The reliability of the crimped foil pyrolysis method itself was verified with highly reproducible replicates of polystyrene Mw 2600 amu. Application of this technique to different ages and reacted versus unreacted zones of AP-based propellants resulted in high variation in the replicates. The variability was so high as to preclude differentiation of two different zones or ages of the same propellant formulation.

A cryogenic crushing procedure was implemented to yield a fine powder from the shavings of propellant and, therefore, deliver a more homogenous matrix. Pyrolysis of this more homogenous finely divided matrix did not demonstrate any improvement over the former shavings pyrolysis for a given zone or age of propellant.

A freshly formulated AP-based propellant, Hipel, was subjected to replicate pyrolysis to ascertain if propellant aging was contributing to the irreproducibility of

pyrolyses. The aging process involves surface oxidation and other chemical reactions yet to be revealed which alter the aged propellant so that visually the outer surface ( reacted zone) is darkly discolored from the inner material (unreacted zone). A representative sample of aged propellant could be difficult to obtain. The fresh propellant should be a fairly homogenous matrix. However, pyrolysis of the Hipel did not yield tighter variations about the average areas.

A modification to the pyrolysis foil crimping was attempted that would control the crimping pressure, i.e. the contact of the sample to the foil surface, and introduce a gas conduit for the pyrolyzate gases. The opinion was strongly held that the abundance of ammonium perchlorate in the propellant could influence the pyrogram adversely by causing additional oxidation reactions. These side reactions might be reduced if the gases could freely leave the foil surface. No improvement with this modification was realized. It was becoming apparent that the presence of an oxidizer in the matrix being subjected to pyrolysis was possibly compromising the repeatability of the pyrogram. Air or more importantly oxygen is removed by purging from the pyrolysis system to avoid these undesirable oxidation side reactions. However, if the matrix itself contains an abundance of an oxidizer, avoidance of these side reactions could be impossible.

In an effort to reduce the inorganic oxidation and allow the pyrolyzate gases to quickly be swept from the foil, open foil pyrolysis was attempted on a THF extract of the AP-based propellant. The THF extract would preferentially dissolve organics from the AP-based propellant with a minor amount of equilibrium inorganics present in solution. The open foil pyrolysis would allow pyrolyzate gases generated by either fragmentation or thermal desorption to leave the foil as rapidly as possible thereby further reducing the potential for adverse oxidative side reactions. Even at these extremes the pyrolyses of replicates of THF extracts of AP-based propellants was highly variable. Pyrolysis of the organic constituents of the AP-based propellant in THF with no inorganic oxidants was much more reproducible than the THF extracts of the propellant itself. Some variation was observed but was generally attributed to the limited solubility of some of the organic compounds in THF. Consequently it appeared that the inorganic oxidant and not the open foil pyrolysis technique was the main factor contributing to irreproducible pyrolyses. Highly reproducible pyrograms of compounds soluble in IPA verified the reliability of the open foil pyrolysis technique. This further supported the notion that the remaining inorganic oxidants in the THF extract were adversely affecting the pyrogram even under the most efficient pyrolyzate gas removal conditions, i.e. open foil pyrolysis.

Finally, an effort was made to subject the ammonium perchlorate to dissolution and collect the solid "organic" material for pyrolysis. It was hoped that the organics could be isolated from the inorganic oxidant(s) which were the main cause of irreproducible pyrolyses. Aqueous DI water extracts of the AP-based propellants were performed but quantitative removal of the ammonium perchlorate from the diminutive residue could not be verified. It was also understood that the red iron oxide and magnesium oxide, if present, would remain in this solid material after extraction due to limited water solubility of these inorganic compounds. Again no reasonable precision was obtained with pyrograms of these solid residues and this was attributed to the inorganic oxidants left in the material.

Both crimped foil pyrolysis and open foil pyrolysis demonstrated good precision when applied to strictly organic matrices. In any pyrolysis technique involving the propellant large variations were observed from replicate to replicate. These variable results were attributed to the presence of inorganic oxidants which could not be completely isolated from the organics. Some equilibrium inorganics would be present in a THF extract or remain in the solid residue after an aqueous extract.

In addition, these sample type preparations were performed more to isolate the reproducibility problem to the AP-propellant inorganic content and not as a viable method of pyrolysis for discriminating between propellant zones and ages. The propellant sample does not completely dissolve in either water or organic solvent and whichever phase is pyrolyzed would no longer be representative of the intact material. These dissolution processes could inexorably alter the subtle chemical changes involved with aging.

When a propellant ages some chemical bonds are cleaved allowing some chemicals to migrate from the bulk material as bleed. Along with bond cleaving, cross linking can occur which hardens the material. The aging propellant changes slightly in chemical composition as well as bond distribution. Determination of these changes seemed well suited to pyrolysis, which fragments materials on the basis of bond strengths. Even the thermal desorption process in pyrolysis could pick up changes in abundance of compounds. However, due to the large presence of inorganic oxidizers these subtle changes were masked by large variations in the repeatability between replicates of a given material. Sample preparation involving solvents would discriminate the matrix on the basis of solubility. Potential bond breaking during the solvation process could result in a pyrogram with a chemical signature non-representative of the original propellant. Analysis of the propellant as the original solid with no sample preparation, which might destroy important chemical information, was the strength of pyrolysis. This particular sample matrix was not amenable to pyrolysis due to the existence of inorganic oxidizers.

## References

1. Druet, Linda M., Shamsuddin Ahmed and Raj N. Pandey, "Application of Curie Point Pyrolysis-Gas Chromatography for the Characterization of Rocket Propellants", Defence Research Establishment Valcartier.
2. Wampler, Thomas P., "Introduction to Pyrolysis-Capillary Gas Chromatography", Journal of Chromatography A, 842 (1999) 207-220.
3. Druet, Linda M., Degenhardt, Carla A. E. M., "Development of a Pyrolysis-Gas Chromatographic Method for Characterization of Plastic-Bonded Explosives", Propellants, Explosives, Pyrotechnics, 15 (1990) 14-18.
4. Burns, Frank B. and Rodacy, Philip J., "A Curie Point Pyrolysis-Dual FSOT Capillary Column Gas Chromatographic System I. Conception and Design", Sandia National Laboratories Report SAND87-0554, Albuquerque, NM (May 1987).
5. Venema, A. and Veurink, J., "A New Method for the Solvent-Free Application of Polymers and Inorganic Materials to Ferromagnetic Wires Used for Pyrolysis-Capillary Gas Chromatographic Studies", Journal of Analytical and Applied Pyrolysis, 7 (1985) 207-213

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