SIZE EXCLUSION HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF A CELLULOSE ACETATE-AMMONIUM NITRATE GAS GENERATOR PROPELLANT

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ABSTRACT

Problems involving mix-to-mix reproducibility for TAL-704 (a Talley Industries of Arizona cellulose acetate-ammonium nitrate gas generator propellant), led to the rejection of several mixes. As a result, a series of studies were initiated to determine the causes of these problems. One such study involved semiquantitative, size exclusion high performance liquid chromatography (SEHPLC) analysis of TAL-704 and its components. A comparison of SEHPLC results for acceptable versus failed mixes of TAL-704 showed that:

1. Each mix sample analyzed exhibited five (5) characteristic peaks with correspondingly similar retention volumes (measured by both ultraviolet and refractive index detectors). These peaks were mainly attributed to cellulose acetate (5.51 ml), dinitrophenoxy-ethanol (DNPE) dimer (8.62 ml), DNPE monomer (9.16 ml), DNPE impurity (9.75 ml), and 4-phenylmorpholine (10.11 ml) respectively;
2. The majority of the mix components analyzed contained one or more impurities in significant amounts (greater than $>1\%$);
3. Analyses of components, for which lot changes had been made between acceptable and failed mixes, revealed that both the DNPE and the 4-phenylmorpholine contained proportionally greater quantities of impurities.

While it was not possible to accurately quantitate the impurities due to the lack of pure material standards, the presence of these impurities in TAL-704 components could account for the lack of repeatability of propellant performance. This technique is presently under further development.

INTRODUCTION

There have been occasional problems associated with the mix-to-mix reproducibility for TAL-704 (a Talley Industries of Arizona cellulose acetate-ammonium nitrate gas generator propellant). Although the various facets of this problem have been studied extensively, this paper describes only one phase of the investigative effort.

The purpose of this study was to semiquantitatively analyze both acceptable and failed TAL-704 propellant mixes and their components, by means of size exclusion high performance liquid chromatography (SEHPLC), in an effort to detect any significant compositional differences between passed and failed mixes.

EXPERIMENTAL

Sample preparation

The following solvents were tested to determine which would most completely dissolve TAL-704 propellant and each of its components:

1. Acetone
2. Acetonitrile
3. Carbon Tetrachloride
4. Cyclohexane
5. Hexane
6. Methylethylketone
7. Tetrahydrofuran (THF)
8. Toluene
9. Trichloroethylene

Of the solvents tested, it was found that acetonitrile and THF produced the optimum results. Due to column/solvent compatibility considerations, THF was selected as the mobile phase, as well as the sample solvent for the majority of the analyses.

TAL-704 propellant mixes

Solutions of approximately 2% sample by weight were prepared by dissolving 2.0 grams propellant drillings in 100 ml THF. These solutions were vacuum filtered through a 1 inch bed of powdered 4A molecular sieve on a fine fritted glass crucible to remove undissolved carbon black and other suspended solids. It should be noted, that filtering through molecular sieve might unintentionally cause the partial or complete removal of certain propellant components other than the carbon black. Prior to injection into the liquid chromatograph, the samples were filtered through a Fluoropore filter (Water's sample clarification kit) to remove all particles larger than 0.5 microns.

TAL-704 propellant mix components

Samples of each TAL-704 component (Table 1), except carbon black and ammonium nitrate, were dissolved in 100 ml THF in approximately the same proportions by weight as in the propellant mixes (weight used, based on 2.0 grams propellant per 100 ml THF). Prior to liquid chromatograph injection, these solutions were filtered through a Fluoropore filter.

TABLE 1. TAL-704 Propellant Mix Components

Component	Formula	Molecular Weight, g	Function in TAL-704
Ammonium Nitrate (AN)	NH_4NO_3	80.05	Oxidizer
Acetyl TriethylCitrate (citroflex A2)	$C_{14}H_{22}O_8$	318.4	Plasticizer
Cellulose Acetate (CA)	$(C_{12}H_{16}O_8)_n$	75,000 avg (polymer)	Binder/fuel
Dinitrophenoxy-ethanol (DNPE)	$C_8H_8N_2O_6$	228.2 (monomer)	Burn catalyst
Carbon Black	C	12.1	Filler/opacifier
Sodium Barbiturate	$NaC_4H_3N_2O_3$	150.1	Slope suppressor
Toluene-2,4-diamine	$C_7H_{10}N_2$	122.2	Acid scavenger
4-phenylmorpholine	$C_{10}H_{13}NO$	163.2	Acid scavenger
Ammonium oxalate	$C_2O_4H_8N_2$	124.1	Coolant
Triethyl Citrate* (citroflex 2)	$C_{12}H_{20}O_7$	276.3	Used to seal propellant to CA cup

* not in propellant mix

Molecular weight standards

Molecular weight (MW) standards (Table 2) were prepared by dissolving 0.10 g of known molecular weight materials in 50 ml THF. In addition, a mixture containing 0.10 g of each MW standard in 200 ml THF was prepared and used to establish degree of separation between standards. Molecular weight resolution was found to decrease as molecular weight increased. Any solution which appeared to contain suspended particulate matter was filtered through a Fluoropore filter prior to injection. Injection volumes ranged from 1 to 20 microliters.

TABLE 2. Molecular Weight Standards

Compound	Molecular Weight, g	Elution volume, ml
Trichloroethylene	131.4	10.44
1-chloro-2,4-dinitrobenzene	202.6	9.66
Dithizone	256.3	9.18
Phenolphthalein	318.3	8.80
Thymolphthalein	430.5	8.66
Waters Associates Polystyrene Standards:		
#26971 - lot 12C	2,350	7.29
#25169 - lot 61110	3,600	7.02
#41984 - lot 50124	233,000	5.57

Molecular weight calibration curve

Molecular weight standards ranged from 130 to 3600 g/mole. A calibration curve was prepared by plotting elution volume vs. MW on semi-log paper. Not included on the calibration curve was a 233,000 MW standard, which was run to determine elution volume of a totally excluded species.

Size exclusion liquid chromatography

Size exclusion high performance liquid chromatography was performed on a Waters Associates Series 200 liquid chromatograph equipped with a Model 440 ultraviolet (UV) absorbance detector (254 nm wavelength cell and photodetector assembly), a Model R401 differential refractometer, a U6K universal injector, a Model 6000A solvent delivery system, and a 30 cm x 7.8 mm Waters 500 Å μstyragel column (for separation of compounds in the 50 to 10,000 MW range). Results of all analyses were recorded on a Perkin-Elmer Sigma I data processor/plotter interfaced with the Waters chromatograph.

Experimental parameters and instrument settings

mobile phase - THF
isocratic flow rate - 1.0 ml/min.
column temperature - ambient
system pressure - approx. 100 psi
sample injection volume - 1 to 40 microliters
UV detector sensitivity - 1.0 and 2.0
RI detector sensitivity - 16 X

Sigma I method parameters

data run time - 15 min.
area sensitivity - 100
baseline sensitivity - 6
attenuation - 0
chart speed - 20 mm/min.

Propellant acceptance tests

TAL-704 mix 631 passed all phases of the three propellant acceptance tests (K_n motor test, Batch check motor test, Lot acceptance test). TAL-704 mix 628 failed the burn rate portion of the Batch check motor test at all pressures tested.

RESULTS AND DISCUSSION

Size exclusion high performance liquid chromatography (SEHPLC) analyses of TAL-704 mixes 628 (failed mix) and 631 (passed mix) were performed using both an ultraviolet (UV) absorption detector and a refractive index (RI) detector. The two, in series units, were used to assure the detection of all significant components. The results of these analyses showed that each propellant mix exhibited five characteristic peaks with correspondingly identical elution volumes (Figures 1 and 2).

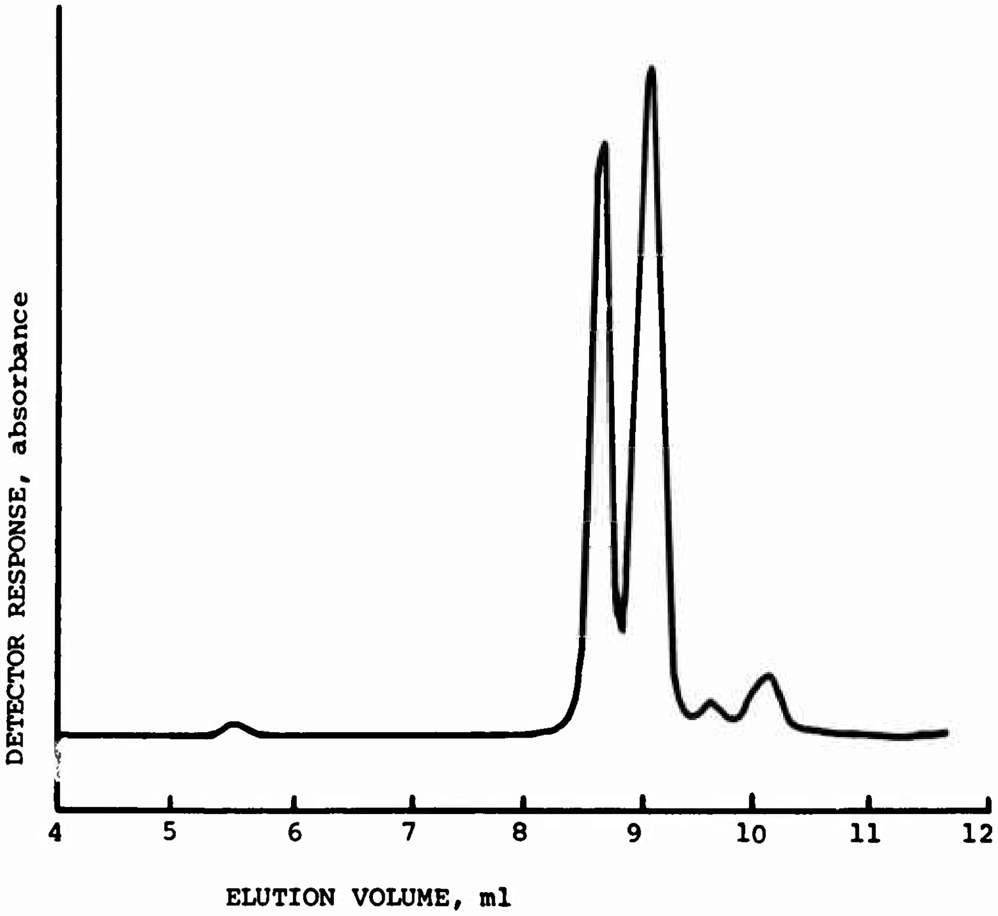

Fig. 1. TAL-704, Mix 631 - SEHPLC using UV detector

These volumes ranged on an average from 5.51 ml to 10.11 ml for the UV detector, and from 5.55 ml to 10.81 ml for the RI detector (Table 3). Each TAL-704 component (Table 4), with the exception of carbon black and ammonium nitrate, was also analyzed by means of SEHPLC using either a UV or RI detector or both. By comparison of mix peak elution volumes to component peak elution volumes, each propellant peak was matched to one or more corresponding component peaks (Table 3). Thus, identification of the five characteristic propellant peaks was achieved. In addition, approximate molecular weight information was obtained for mix and component peaks (using UV detector only) by obtaining elution volume data for a series of molecular weight standards (130 to 3600 MW range) and plotting a standard curve. This information was useful in differentiating component peaks from impurity peaks in the analyses of the various mix components.

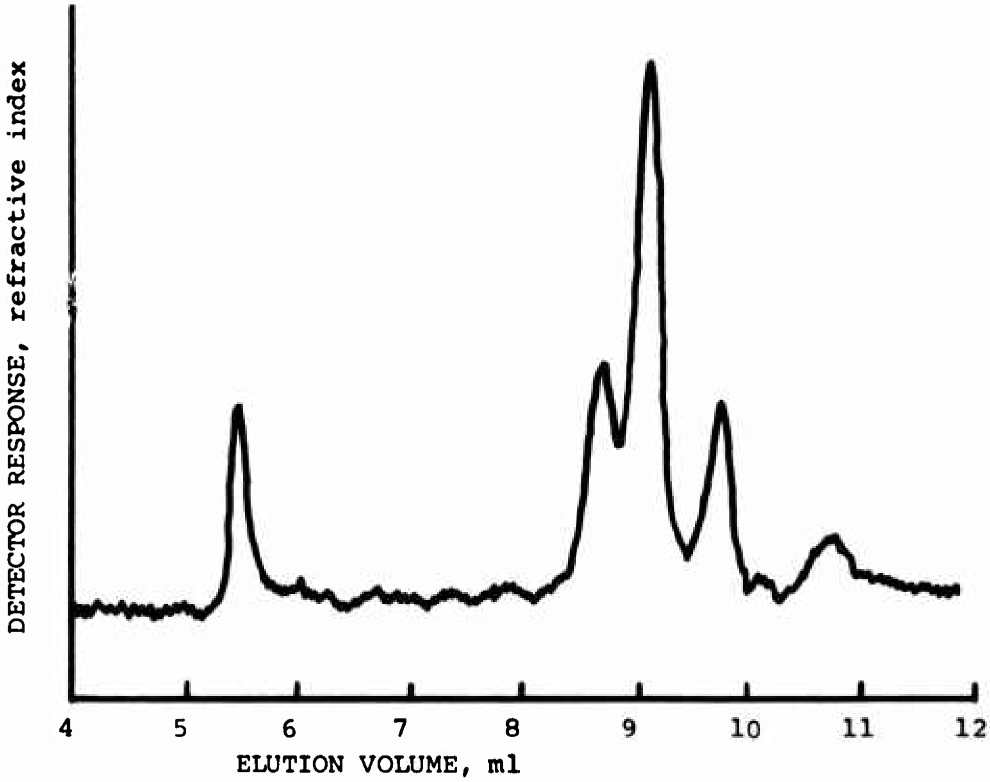

Fig. 2. TAL-704, Mix 631 - SEHPLC using RI detector

UV detector

A comparison of the average characteristic peak areas for the TAL-704 mixes in THF, as well as acetonitrile, showed a few minor differences between the failed and passed mixes (Table 3). In each case, a ratio of peak 3 to peak 2 showed that the area of peak 3 was slightly larger than the area of peak 2 for mix 631 (1.20:1.00), whereas for mix 628, the peak areas were almost identical (1.01:1.00). Based on the results of component analyses and considering factors such as detector sensitivity, sample size, signal attenuation and component concentration in the mix, it was determined that the differences observed are mainly due to variations in the monomer/dimer content of the dinitrophenoxyethanol (DNPE) constituent. The fourth peak, which was identified as predominantly a DNPE impurity, was approximately 1.5% greater in area for the failed mix than for the passed mix. While the increased amount of impurity associated with the burn catalyst, DNPE, in mix 628, could be a contributing factor to that mix's failure of certain acceptance tests, it is not considered significant. Peaks 1 and 5, which were identified as cellulose acetate (CA) and 4-phenylmorpholine respectively, were in all cases nearly invariable in area.

Analysis of the various TAL-704 components showed that few were pure substances, and that several, for which a lot change had been made between passed and failed mix. For example, as previously stated, the DNPE impurity peak was approximately 1.5% greater for the failed mix. Also, the 4-phenylmorpholine displayed an impurity shoulder for the failed mix, which was not present with the passed mix. Although

TABLE 3. SEHPLC Results For TAL-704 Propellant Mixes

			UV DETECTOR		PEAK IDENTIFICATION	
Sample, Mix No.	Peak No.	Elution Volume, ml	Approx. Percent Peak Area	*Approx. Molec. Weight, g	Major Component	Minor Component(s)
628	1	5.51	<0.1	> 20,000	Cellulose Acetate	
	2	8.62	44.1	345	DNPE dimer	
	3	9.16	44.4	265	DNPE monomer	citroflex A2 sodium barbiturate
	4	9.75	4.2	195	DNPE impurity	citroflex A2 toluene-2,4-diamine
	5	10.11	7.4	160	4-phenylmorpholine	
631	1	5.52	<0.1	> 20,000	cellulose acetate	
	2	8.62	40.9	345	DNPE dimer	
	3	9.17	49.1	265	DNPE monomer	citroflex A2 sodium barbiturate
	4	9.75	2.7	195	DNPE impurity	citroflex A2 toluene-2,4-diamine
	5	10.11	7.3	160	4-phenylmorpholine	
			RI DETECTOR			
628	1	5.56	11.7	**	cellulose acetate	
	2	8.68	23.2		DNPE dimer	
	3	9.23	45.6		DNPE monomer	citroflex A2
	4	9.82	10.9		DNPE impurity	citroflex A2 4-phenylmorpholine impurity
	5	10.81	8.6		4-phenylmorpholine	
631	1	5.54	12.3		cellulose acetate	
	2	8.73	16.0		DNPE dimer	
	3	9.23	49.8		DNPE monomer	citroflex A2
	4	9.81	14.4		DNPE impurity	citroflex A2 4-phenylmorpholine impurity
	5	10.80	7.5		4-phenylmorpholine	

* From MW calibration curve

** No MW calibration curve run for RI Detector

TABLE 4. SEHPLC Results For TAL-704 Mix Components

Sample Mix Component	Peak No.	MIX 628 Elution Volume, ml	MIX 628 Approx. % Peak Area	MIX 628 *Approx. Molec. Wt., g	MIX 631 Elution Volume, ml	MIX 631 Approx % Peak Area	MIX 631 *Approx. Molec. Wt., g
			UV DETECTOR				
DNPE	1	8.62	45.7	345	8.62	45.2	345
	2	9.16	52.3	265	9.16	53.7	265
	3	9.74	2.0	195	9.72	3.1	200
Citroflex A2	1	9.16	57.6	265	No lot number change		
	2	9.75	42.4	195	No lot number change		
4-phenylmorpholine	sh	9.62	≈10.0	205	-		
	1	10.12	≈90.0	160	10.11	100.0	160
Sodium Barbiturate	sh	9.15	85.0	265	Not run		
	1	9.20		260			
	2	11.36	15.0	82			
Cellulose Acetate	1	5.51	100.0	>20,000	5.52	100.0	>20,000
Toluene-2,4-diamine	1	9.71	100.0	200	No lot number change		
Ammonium Oxalate	1	9.24	76.4	250	No lot number change		
	sh	9.30		245			
	2	11.39	23.6	81	No lot number change		
Citroflex 2	1	9.17	15.2	265	Not run		
	2	9.77	80.4	190			
	3	10.10	4.4	160			
			RI DETECTOR				
DNPE	1	8.71	23.2	**	8.68	23.9	**
	2	9.23	32.7		9.10	35.0	
	3	9.83	44.2		9.80	41.2	
Citroflex A2	1	9.20	46.2		No lot number change		
	2	9.82	53.8		No lot number change		
4-phenylmorpholine	1	9.86	66.6		9.86	72.6	
	2	10.85	33.4		10.85	27.4	
Citroflex 2	1	9.10	38.9		Not run		
	2	9.82	35.4				
	3	10.80	25.8				

* From MW calibration curve
** No MW calibration curve run for RI Detector
sh = shoulder

the Citroflex A2 (TAL-704 component) and Citroflex 2 (cellulose acetate cup/ propellant sealer) lot numbers were not changed from failed to passed mixes, SEHPLC analysis indicated that both materials contained significant amounts of impurities. In addition, the analyses of the sodium barbiturate and ammonium oxalate components also showed the presence of impurities as shoulders or as separate peaks. In all cases, the identification of a peak or shoulder as an impurity was based on the magnitude of the peak and the approximate molecular weight it represented.

RI detector

To augment the SEHPLC-UV detector findings, a smiliar series of mix and component analyses were run utilizing a refractive index detector. The use of this second detector assured the detection of any major or minor components which do not absorb in the UV at 254 nm. As with the UV detector, analyses of the propellant mixes again produced five characteristic peaks (figure 2); but with slightly larger elution volumes resulting from the downstream position of the RI detector relative to the UV detector. Also, because differences in refractive index are being measured, rather than UV absorption, peak area ratios are considerably different than those determined using the UV detector.

The results of peak identification for the propellant mixes (Table 3), based on elution volume data for the various TAL-704 components, was the same as obtained using the UV detector, with the exception of peak 4. This peak. identified as predominantly a DNPE impurity, was also attributed, in a small part, to a 4-phenylmorpholine constituent not visible with the UV detector. The results for DNPE analyses using the RI detector confirm the findings obtained with the UV detector, in that the impurity attributed to the third peak was found to be slightly greater for the failed mix than the passed mix. However, area analysis of peaks 2 and 3 indicated there was a 3:1 monomer:dimer ratio (ratio of peak 3 to peak 2 - Table 3) for the passed mix vs. a 2:1 monomer:dimer ratio for the failed mix. This was somewhat different than the results obtained with the UV detector. In addition, the presence of several impurities in the Citroflex A2 and Citroflex 2 was verified by means of the RI detector.

CONCLUSIONS

Due to the inavailability of pure materials for standards, it was not possible to accurately quantitate the SEHPLC results presented here; however, by means of a two detector system, several potentially useful discoveries, regarding TAL-704 propellant and mix components, were made on the semi-quantitative and qualitative levels.

1. It was shown that there are one or more impurities present in the majority of the TAL-704 mix components analyzed.

2. For at least two of the components (DNPE and 4-phenylmorpholine), whose lot numbers differed between passed and failed mixes, there were proportionally greater quantities of impurities present with the failed mix.
3. A significant difference in the Monomer/Dimer ratio for the DNPE content suggests that DNPE preprocessing to control that ratio may improve reproducibility of formula characteristics.

The results of this study clearly indicate that further analyses of TAL-704 and selected components are necessary; and that an effort should be made to identify, quantitate and control the impurities which may determine propellant performance.