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DEVELOPMENT OF ANALYTICAL TECHNIQUES FOR
LIQUID PROPELLANT SURVEILLANCE

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<p>The U.S. Army has made a commitment to develop liquid gun propellants as a potential replacement of solid propellants used in the 105-mm and 155-mm guns. The stability and therefore integrity of these propellants, after being stored for extended periods of time, is necessary in order to meet ballistic requirements. The long-term storage of liquid propellants is required to determine whether there is any instability; its cause; and, if necessary, its prevention. At this time failsafe criteria is not available for liquid propellants under long-term storage conditions. A methodology is being developed to establish this criteria.</p> <p>Analytical methods have been developed to provide the means to monitor these long-term storage studies. Previously developed techniques for this program were reviewed and those which were applicable for this program were investigated. The investigation led, in some cases, to revisions and new developments to permit analysis of major ingredients, contaminants, and degradation products. All of the methods selected were tested in-depth, and with several, comparison studies were conducted. As a result, a capability is available to monitor liquid propellants during storage, to establish kinetics and decomposition mechanisms, to establish specifications, and to permit evaluations of additives.</p>						
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INTRODUCTION

The logistical, ballistic, cost savings advantages and liquid propellant features have prompted an extensive program for the characterization of liquid propellants. Liquid propellants have been categorized as an insensitive munition (ref 1). They are presently under consideration as a potential replacement of solid propellants for the 155-mm howitzer gun.

Establishing the integrity of these propellants after being stored for extended periods of time is necessary to assure that the fail-safe criteria are met. The fail-safe criteria of this program are defined as safety, storability, and ballistics. In order to establish these criteria studies are required to determine aging effect on the stability and storability of liquid propellants. To facilitate the acquisition of data, accelerated temperature testing is being employed. The rate data generated in these experiments is being used for determining the various fail-safe criteria for liquid propellants. This information will also be used to establish a long-term storage plan and the design of containers for this study. Ultimately, a manual will be written outlining limitations on storage of liquid propellants, safety factors, and effects on ballistics.

The use of liquid propellants in diverse gun applications necessitates extensive characterization of the propellant system. This requirement has resulted in the evaluation and development of analytical methodologies. These techniques will provide the capability to monitor the composition of liquid propellants in storage. Several important features which were considered for candidate techniques included reproducibility, reliability, simplicity, safety, and environmental impact.

BACKGROUND

The propellant systems currently under investigation are stoichiometric mixtures of hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN) in water. A typical composition, LP 1846, has 61% HAN, 19% TEAN and 20% water. For this mixture the molar ratio of HAN to TEAN is 7:1 which is stoichiometric for conversion to carbon dioxide, water, and nitrogen. The liquid propellant composition LP 1846 is the prime candidate currently under consideration.

Determining the effects of temperature and contaminants on the stability of liquid propellants and providing analytical techniques for monitoring liquid propellant before and after exposure to these variables is necessary. Analyses are required for identification and quantitation of major propellant components, contaminants, and degradation products to provide a basis for establishing the various criteria. The criteria of interest include decomposition kinetics and mechanisms, propellant composition, and ballistics-relationships, product specifications, pressure build-up during long-term storage as well

as propellant shelf-life and safety factors. Low level concentrations of contaminants or impurities have been identified previously (refs 2 and 3) such as nitrates, acids, amines, NO_x and trace amounts of transition metal ions. This list is not considered to be complete until this investigation has been concluded.

PROCEDURE

A review of techniques was presented in previous reports (refs 2 and 3). In-depth studies were conducted to confirm reliability and to optimize several of the techniques.

The titrimetric method for HAN and nitric acid using a metrorohm model E536 potentiograph and a model 655 dosimat was optimized for titrant type and sample size.

A feasibility study was successfully completed for the analysis of HAN, TEAN and AN by supercritical fluid chromatography (SFC) using a suprex system. This system will be optimized at a later date.

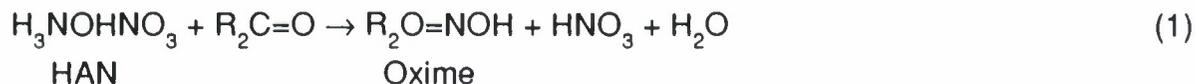
Metals analyses were conducted and compared on several systems including polarography, graphite furnace atomic absorption spectrophotometry (GPAA), inductively coupled plasma spectrophotometry (ICP), inductively coupled plasma spectrophotometry/mass spectrometry (ICP/MS) and ion chromatography (IC). The data in this report were obtained on an E G & G PAR model 384 polarograph, on a Perkin Elmer Zeeman/5100 GPAA, on both a Perkin Elmer's (Plasma II) and an ARL (Model 3510) ICP's, on a Perkin Elmer's Elan 500 ICP/MS and on a Waters' IC. Optimizations studies will be conducted on one or more of these techniques.

RESULTS AND DISCUSSION

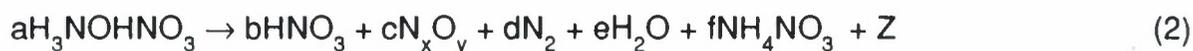
Several of the analyses have received considerable attention due to their complexity and necessity for accurate results. The determination of both free nitric acid and of hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN) is an area that has experienced some difficulty. In-depth investigations of the use of titrimetry as well as alternative techniques such as ion and supercritical fluid chromatography have been conducted.

A titrimetric method developed by Dr. Kasler at the University of Maryland was reviewed as a potential technique for HAN/TEAN analysis (refs 4 and 5). This method used methyl isobutyl ketone to convert HAN to a stronger acidic product, nitric acid, to separate it from TEAN. TEAN, which is a weak acid, is not affected by the ketone and

is easily differentiated in the titration curve. The actual titration is based on the nitric acid liberated during the formation of an oxime. The oxime which is a very weak acid ($K_b < 10^{-12}$) is not titrated.



HAN based liquid propellants can undergo decomposition as a result of the presence of various contaminants. Nitric acid and transition metals are among those which most affect the stability of liquid propellants. Some of the numerous products which may be formed during decomposition are shown in equation 2:



The actual mechanism for liquid propellant decomposition proposed in equation 2 will be established by gas and liquid phase analyses of experimentally aged samples. Nitric acid formation during decomposition poses a serious problem in the stability of the liquid propellant and must be accurately monitored. Free nitric acid can be introduced as a product of decomposition or from production as a residual contaminant. Therefore, this titrimetric method will result in erroneously high HAN values in samples with significant decomposition or with residual acid from production. As a result a capability was required to determine free nitric acid separate from nitric acid produced in the ketone/HAN reaction. This was accomplished by performing two titrations. First, the sample was titrated for free nitric acid from production and/or decomposition. This was accomplished by eliminating the ketone from the sample solvent. This causes the HAN to remain unchanged. The free nitric acid from HAN decomposition or propellant production could then be titrated. This is possible since the HAN and TEAN, which are very weak acids, form one break in the titration curve after the stronger, free nitric acid break (fig. 1). Tetrabutylammonium hydroxide 0.01N in methanol was used as the titrant with 50 ml of ethanol as the sample solvent. Since this discussion is involved with monobasic acids and bases, normality and molarity are equivalent and are used interchangeably. In order to provide the necessary accuracy for concentrations of $\text{HNO}_3 < 0.5\%$ a 0.6 gram sample was chosen; and for concentrations of $\text{HNO}_3 > 0.5\%$ a 0.3 gram sample is required (refs 2 and 3). Finally, the HAN/TEAN is determined in a separate titration with the addition of ketone to the sample solvent for HAN conversion.

A comparison of the aqueous versus nonaqueous free nitric acid titrations led to the selection of the nonaqueous method. The overall standard deviation of both methods was comparable with the aqueous at $> \pm 0.02$ and the nonaqueous at $< \pm 0.02$ (tables 1 and 2). The titration curves for the nonaqueous method were more symmetrical, less noisy and more sensitive. The choice of sample weight was also critical. In keeping with acceptable titration technique as prescribed by numerous authors as well as safety

and environmental directives, sample size was kept minimal. The effect of sample concentration is vividly expressed in figure 2 where percent recovery is dramatically reduced as sample concentration is increased. The calculations for figure 2 were made without subtraction of the solvent blank in order to show the effect of large samples. The actual recovery of nitric acid added as shown in table 1 is a complete loss or zero recovery with sample sizes greater than one gram.

The choice of this method or any other method as well as methods for HAN and TEAN was restricted by the amount of sample available. As a result of laboratory safety regulations and restrictions on maximum sample quantities allowable, accelerated exposure studies and long-term storage studies had limitations on the amount of sample which could be used. Due to these limitations and directives to reduce waste and sample usage, analytical methods had to be tailored to comply with these restrictions. This is not an unrealistic limitation. Regardless of whether the application is research or in the final stages of actual field usage, it is most practical to limit any energetic sample quantity for testing. Therefore, the creations of these techniques under strict compliance directives will have greater potential for future applications.

The original HAN/TEAN method by Kasler produced titration curves which, although the breaks were apparent, were not sufficiently discernible for the accuracy required to meet the criteria of this program. The most desirable output was the first derivative curves which provided more easily defined end points. Substituting acetone for the higher ketones used by other investigators (refs 3 and 4) to convert HAN to nitric acid led to titration curves with sharper, noise free end-points. Also, to achieve the desired results, large samples were used with pre-addition of titrant to reduce analysis time and provide accurate data. These large samples (0.6 g) were still within accepted levels for ionic strengths of less than 0.1 (eqs 5 through 7). To maintain the sensitivity and applicability of the titration curves, the titrant used was also important. Of those tested, tetrabutyl ammonium hydroxide (TBAH) was consistent with this requirement. TBAH was found to be applicable to both the nitric acid and HAN/TEAN analyses although n-butylamine in methanol was the preferred titrant for free nitric acid from degradation and production. The use of the two titrants was not pursued as it was expedient to use only one titrant since both gave comparable results. The titrant for the HAN/TEAN analytical method is 0.2N TBAH in methanol. The sample size is 0.6 gram with pre-addition of 15.0 ml of titrant in 50 ml of ethanol/acetone (100:1) (ref 2 and 3).

Blank values were determined for all reagents. The effect of the reagent used as a diluent or solvent was in some cases quite significant. A tabulation of these data are shown in table 2. Calculation of the blank as a nitric acid shows that a significant error would be introduced in the case of ethanol 2.

A study was also conducted comparing the aqueous versus nonaqueous titration of two liquid propellant lots (table 4) and of a synthetic lot using hydrochloride standards (table 5). Both LP-2 and LP-3 are lots which originally passed HAN specification quality

control which is $60.8 \pm 0.5\%$. Using this as a basis the results in table 4 indicate that the nonaqueous titration provides more realistic results. This is confirmed further with the data in table 5. In this case pure hydrochloride standards were used to prepare solutions containing the same amount of cation (hydroxylamine or triethanolamine) which would be present in the nitrate solutions of LP 1846. Again, the nonaqueous determination resulted in closer agreement with actual concentration of HAN. The TEAN results are not as relevant in this discussion since very small amounts of low molecular weight, weakly acidic impurities will have a significant effect on the TEAN concentration. Also, slight differences in titrant volume have a very significant effect on the TEAN content detected. Due to the many difficulties with the TEAN titration, its results are only used as an indicator. Reliance will be made on the chromatographic techniques for accurate TEAN results. The only interesting observation in the TEAN comparison is that the aqueous titration results in higher TEAN concentrations. This may be due to unreacted HAN which would account for low HAN values. If one considers the effect of molecular weight from equation 3, any unreacted HAN (MW=96) would have more than a two-fold effect on increasing the percent TEAN (MW=212) detected. Considering the role of molecular weight in the titrimetry calculations, the presence of a species of lower molecular weight would increase the calculated amount detected (equation 3) as shown in example.

$$\%X = \frac{(100) [(ml \text{ titrant}) (N \text{ titrant}) (MW/1000)]}{Spl \text{ Wgt, g}} \quad (3)$$

Example: Calculating unreacted HAN as TEAN with TEAN.

1. Volume (2% unreacted HAN) = 0.5 ml; 2. for TEAN=2.2 ml.

Result: a. %TEAN (HAN) = $[(100) (0.5) (0.2) (0.212)]/0.5 = 4.2\%$

b. %TEAN = $[(100) (2.2) (0.2) (0.212)]/0.5 = 18.7\%$

% TEAN would calculate as 22.9% or >20% error.

In order to provide an analytical capability, an overall review and understanding of basic principles of the methods employed is necessary. One of the approaches, titrimetry, which has been chosen for characterizing the major components and the nitric acid contaminant in liquid propellants is one of complex dimensions. Titrimetry in either aqueous or nonaqueous media is often neither simple or well defined and must be used with an understanding of its limitations. For this particular application, nonaqueous potentiometric titrimetry was selected for reasons which will be enumerated.

The selection of nonaqueous over aqueous titration methods provides increased sensitivity of weakly acidic species such as TEAN. That is, the amplitude of the derivative curve is greater and much sharper. In the case of strong acids or bases the titration curve break in aqueous media is sufficiently distinct for accurate determinations. But, "the titration in ethanol of an uncharged acid, like acetic or benzoic, gives the same

break in pH at the equivalence point as the titration in water. The dissociation constant of the acid is 10^{-6} times as large in ethanol as water... An uncharged acid with a dissociation constant of 10^{-11} in ethanol gives the same break at the end point as an acid with a dissociation constant of 10^{-5} in water." This holds true for all acids and bases (ref 6). This property of nonaqueous titrations was evidenced in experiments with liquid propellants in not only sensitivity but sharpness of the curves. A similar type of applications was alluded to by Kolthoff and Elving in which they reported, "The acid ammonium ion is too weak an acid in water to be determined accurately by direct potentiometric or visual titration with an indicator. However, in ethanol it has a dissociation constant of the same order of magnitude as that of benzoic acid, and it can be titrated very sharply. Much use of this effect is made in the titration of cation acids, especially of the organic type, including the charged amino group in amino acids." (ref 6). By careful observance of titrant and solvent effects and the increased sensitivity of nonaqueous media, it was possible to qualitatively and semi-quantitatively distinguish between weakly acidic species, TEAN and AN. This characteristic has been observed by others in ethanol and other nonaqueous media.

To be consistent with general practices set forth by numerous investigators, a dilute system was considered as an optimum approach. Bates and others state that by most standards no quantitative interpretation of measured pH values should be attempted unless the medium can be classified as a dilute solution of simple solutes with ideality approaching ionic strengths less than 0.1 (ref 7). These criteria are fulfilled by both nonaqueous methods which were developed (equations 5 through 7). Concentrated solutions create large changes in activity coefficients and buffering affecting the shape of the titration curves (refs 6 and 8) which was evidenced in recent studies of percent recovery of nitric acid with sample size (fig. 2). Since buffering capacity is the property of a solution to resist pH change, it is a requisite, especially in analyses which require monitoring traces or slight changes, to reduce buffering power through dilution. Evidence of buffering as a result of concentrated samples is illustrated in the derivative curves of figures 3 through 6. A standard symmetrical nonaqueous titration is illustrated in figure 3, and the effect of a larger sample in which the curve becomes very noisy and shallow is shown in figure 4. The effect of increasing sample size using the aqueous method whose curves are asymmetrical, is shown in figure 5. As sample size was increased the curve became increasingly shallow and eventually indiscernible. Figure 6 is an aqueous titration with a very large sample (~30 g) in which the curve is measurable but very noisy and asymmetrical, as shown in figure 6. The agreement obtained between the aqueous and the nonaqueous methods may have been coincidental. It was a deviation from the other concentrated samples which were tried since a discernible break was observed. Nevertheless, the more reasonable approach is with small samples.

Using classical associations and definitions the following relationship exists between pH and pK values:

$$\text{pH} = \text{pKa} + \log(\text{Ab}/\text{Aa}) \quad \text{if } \text{Aa} = \text{Ab}, \text{pKa} = \text{pH} \quad (4)$$

where Aa and Ab are activities (~concentrations).

Since $\text{Aa} = \text{Ab}$ is approximately fulfilled by one-half the endpoint volume, $V_E/2$, the point K on the curve can be easily determined resulting in the appropriate pH from which the corresponding pKa can be found (fig. 7). Although the pKa determined in this manner is not exact it is sufficient for this comparison. The buffering capacity, b, is a differential quantity and can be determined by drawing a tangent to the titration curve (fig. 7). The buffering capacity can also be calculated as $b = DV$ (equiv/l)/DpH. The more symmetrical the curve the more distant b is from the end point. Titrations were run using techniques currently being employed for HAN-based propellants (figs. 8 through 11). Calculations are shown below for several of the aqueous and nonaqueous titration S-curves of LP 1846-03-11 from figures 8 through 11:

Method	End point		b	pK	HNO ₃ (%)	HAN(%)	Start
	ml	ph					pH
Aqueous	0.50	2.08	0.28	1.92	0.03		1.80
Nonaq	1.50	2.17	0.019	1.79	0.07		1.54
Aqueous	15.53	5.04	0.24	1.90		60.29	1.09
Nonaq	13.62	3.15	0.44	~0.30		60.91	-0.35

The data from these calculations show the consistency of this set for percent detected. The most significant observation is the value for the buffering capacity. For HAN analysis both methods use ~0.5 grams and are similar. But, for the titration of nitric acid, there is a very large difference in buffering capacity which would make the aqueous method more susceptible to error. This larger buffering capacity is a function of the larger sample size, 20 to 30 grams, versus the smaller sample for the nonaqueous method (0.5g).

Based on the optimized nonaqueous titrimetry technique, ionic strengths can be calculated to determine conformity with accepted practices. The molarities and therefore ionic strengths which were used for this study for liquid propellant, LP 1846, containing HAN at 8.94M and TEAN at 1.34M are as follows:

Using 0.6 grams of LP or 0.42ml at a density of 1.42,

$$\begin{aligned} \text{HAN} &= \\ \text{ml}[M/(1000\text{ml/L})] &= \text{moles} & (5) \\ 0.42[8.94/1000] &= 0.00375 \text{ moles} \end{aligned}$$

$$\text{TEAN} = 0.42[1.34/1000] = 0.00056 \text{ moles}$$

Diluted in 50ml,

$$\text{HAN} = [(\text{moles} \times 1000\text{ml/L})/\text{ml}] = \text{molarity} & (6) \\ [(0.00375 \times 1000)/50.42] &= 0.074\text{M}$$

$$\text{TEAN} = [(0.00056 \times 1000)/50.42] = 0.011\text{M}$$

Ionic strength, μ ,

$$\mu = 1/2 \sum \mu z^2 & (7)$$

$$1/2[0.074 \times 1 + 0.074 \times 1 + 0.011 \times 1 + 0.011 \times 1]$$

$$0.170/2$$

$$0.085 \quad (\text{Note: Bates (ref 7) prescribed as } <0.1)$$

In the concentrated systems, the curves are more asymmetrical (figs. 3 through 11) which are a function of the buffering capacity maximum, b , being close to the titration end-point. In the symmetrical curves from the dilute systems, the maximums are far removed from the end-point.

Another illustration of buffering as expressed by Kolthoff and Sandell states that in any weakly acidic solutions, HA, the equilibrium is determined by the magnitude of the ionization constant:

$$[\text{H}^+][\text{A}^-]/[\text{HA}] = K_a & (8)$$

and $[\text{H}^+] = \{[\text{HA}]/[\text{A}^-]\} \times K_a$

If one considers a mixture of a weak acid and its salt, KA, it is a strong electrolyte. The concentration of A^- ions sent into solution by the salt is practically equal to the molecular concentration of the salt which represses the dissociation of the acid, HA, since it furnishes the common ion A^- . Frequently this repression is so great that we can consider all of the acid present to be in the undissociated form (ref 8).

Much of the previous discussion has been centered on the overall theory and none on mechanics or electrodes. Among the electrodes which have applicability in non-aqueous media are glass and silver/silver-chloride which have been employed in this investigation. Although the thermodynamics are not clearly defined between solvents, this is not a deterrent to application of this technique. To be meaningful potential measurements much be made relative to a stable reference electrode which is also reversible and unreactive with any other components of the system. The silver-silver

couple fits these requirements since it provides rapid electron transfer; its components are neither strong oxidants nor reductants making it stable and it forms insoluble halide salts making possible the half reactions in equation 9 (ref 9).



$$E_{\text{AgCl/Ag}} = E_{\text{AgCl/Ag}}^0 - (RT/F)\ln(\text{Cl}^-) \quad (10)$$

The reversible potential for this couple in equation 10 is a function of its standard electrode potential and of chloride activity. With a large chloride concentration in the electrode, it is possible to assure that the small current drawn during its use will not affect the reference potential (ref 9). The chloride concentration of 3M KCl (aq) in the inner chamber and saturated LiCl in ethanol in the outer chamber which are not subject to oxidation (ref 9) and are adequately soluble in either water or ethanol. This concentrated salt bridge will essentially provide equal cation and anion mobilities without which it is ordinarily not possible with nonaqueous systems. Regardless of solvent media it is essential to maintain low solution activities through the use of dilute solutions.

During the course of this investigation, it was observed that the break in the titration curve for AN, EAN, and DEAN, which are also weak acids, are not resolved from TEAN (fig. 12). Since these contaminants could have a large impact on the TEAN determination, an alternative method for TEAN was necessary. It was observed also that slight differences in titrant volume had a very significant effect on the TEAN content detected. Since there were many difficulties with the TEAN titration, its results were considered for use only as an indicator. Due to the observed limitations of titrimetry, ion and supercritical fluid chromatography were investigated for the analysis of HAN, TEAN, EAN, DEAN, and AN. This does not preclude the use of titrimetry. Potentiometric titrimetry does appear to provide accurate HAN analysis and an indication of other contaminants in the titration break for TEAN when a first derivative output is used. The use of titrimetry will be continued until either IC or SFC or both are optimized. Both IC and SFC instrument manufacturers (refs 10 and 11) were consulted on the above mentioned analyses which resulted in feasible approaches for further investigation. One of the important considerations which led to SFC was environmental impact and waste disposal.

A capability was developed on IC to separate HAN, TEAN, DEAN, EAN and AN. Current investigation is in progress to determine the precision and accuracy of this technique. Preliminary results indicate that IC is a viable method. An IC-pak TM column and a conductivity detector were used for the separation and detection. A 20-100 μl size sample of diluted liquid propellant (3/5000 in water) was injected using 1-4mM HNO_3 /0-15% methanol as the eluant. The separation using this technique is shown in

figure 13 (refs 2 and 3). The nitric acid molarity affects the speed of elution of the HAN and AN primarily and the methanol concentration, primarily the TEAN. This combination can be used to vary the elution times of the components of interest for a particular application.

As a result of recent progress in the field of SFC, this chromatographic procedure was also reviewed. Conformity to stricter environmental and waste disposal regulations have required a search for compatible techniques which would permit achievement of analytical goals and compliance with these new directives. This method, too, has been shown to provide the desired results and merits further investigation. The chromatographic column used in this separation was 10 cm x 1.0 mm x 5 μ m methyl deltabond with supercritical carbon dioxide plus 0.3% formic acid as eluant. The sample of LP 1846 was extracted on celite with supercritical carbon dioxide plus 0.3% formic acid prior to analysis. The result of the analysis is shown in figure 14 (ref 11).

Another contaminant in liquid propellants which requires accurate detection is the transition metals. The transition metals - especially iron, copper, nickel, chromium and aluminum - are known to accelerate the decomposition of HAN-based propellants. Considerable effort has been expended in this area to provide a reliable technique. Analytical methods which have been considered include polarography, ion chromatography, inductively coupled plasma, atomic absorption (AA), graphite furnace AA and inductively coupled plasma/mass spectrometry.

Initially, polarography was used to develop methods for Cu^{+2} , Ni^{+2} , Fe^{+3} , and Cr^{+6} (ref 3). The ability of the liquid propellant to act as oxidizer, reducing agent or chelating agent for species of the transition metals complicated the polarographic analyses. This fact was made evident when ICP data was compared to polarographic data for iron (table 6). The difference between the two illustrates that most of the Fe^{+3} in the liquid propellant is in a complexed state and not available for polarographic detection as Fe^{+3} (ref 3).

As a result of the difficulties encountered with polarography, IC was investigated and feasibility studies conducted on metal spiked samples of liquid propellant. Preliminary data indicate that IC will provide both quantitative data for all species of interest as well as oxidation states. This information will be useful in determining the role of metal impurities in liquid propellants.

For the ion chromatography of metals a μ Bond pak C18 column with a 2mM NaOS/50mM tartaric acid (pH adjusted to 3.4 with 50% NaOH) eluant at a flow rate of 1.0 ml/min was used. The post column reactant (PAR) flow rate was 0.5 ml/min. An ultra-violet (UV) detector at 520nm was required for the identification of the metals present.

The samples were diluted 1/10 in water, and the injection volume was 100 μ l. The IC chromatogram is shown in figure 15 (ref 10). The top figure is of a metals standard with a range of 0.5 to 1.0 ppm of the +2 transition metals. The lower figure is an actual LP sample containing Fe^{+3} and only slight traces of other transition metals.

The inductively coupled plasma spectrometer and atomic absorption spectroscopy were also investigated. Results from several laboratories indicated that ICP analysis of metals in liquid propellants is not at all straight forward. The levels which were reported on the same sample deviated by as much as 100%. The use of standard AA was insensitive to the levels necessary for this program. After an extensive search, a study was conducted which compared ICP using internal and external standardization with graphite furnace AA (refs 12 and 13). The data from this study is shown in table 7. From this comparison the GPAA would be a good reference technique. This is based on the more simplistic approach used in conducting analyses on the GPAA. Careful use of the ICP with internal standardization will also produce reliable results.

CONCLUSIONS

The final selection of analytical techniques for this program is still under investigation. The uses of titrimetry have been well illustrated as well as the advantages of chromatography. The development of the latter has far-reaching utility and applicability to many facets of this program. For the analysis of metals, besides inductively coupled plasma spectrophotometry and graphite furnace atomic absorption spectrophotometry, ion chromatography is also being considered. Here again, ion chromatography has some very distinct advantages including speed, versatility, and the ability to distinguish between oxidation states. In conclusion, all of these techniques have their advantages and disadvantages and must be weighed for the particular application.

The review of analytical methodologies which are applicable for monitoring the storage of liquid propellants has led to the investigation of many diverse techniques. Any or all of these have applicability for particular requirements. This investigation has endeavored to provide some insight into their advantages and disadvantages.

Table 1. Nonaqueous titration - nitric acid spiking study

<u>Sample</u>	<u>Acid added(%)</u>	<u>Acid present(%)</u>	<u>Total acid(%)</u>	<u>Acid found(%)</u>	<u>Std dev</u>
Ethanol	0.03	0.0	0.03	0.02	0.01
	0.03		0.03	0.02	
	0.05		0.05	0.04	
	0.05		0.05	0.04	
	0.13		0.13	0.12	
LP 1846 no.1	0.0	0.08	0.08	0.09	0.02
	0.0			0.07	
	0.04		0.12	0.10	
	0.04		0.12	0.11	
	0.05		0.13	0.14	
	0.06		0.14	0.17	
	0.14		0.22	0.21	
	0.16		0.24	0.22	
	0.33		0.41	0.43	
	0.33		0.41	0.41	
LP 1846 no.2	0.0	0.11	0.11	0.11	0.02
	0.0			0.11	
	0.06		0.17	0.15	
	0.16		0.27	0.23	
	0.32		0.43	0.41	
LP 1846 no.3	0.0	0.10	0.10	0.11	0.01
	0.0			0.09	
	0.0			0.11	
	0.03		0.13	0.13	
	0.0			0.13	
	0.0			0.13	
	0.0			0.12	
	0.07		0.17	0.17	
	0.0			0.16	
	0.0			0.17	
	0.0			0.16	

Table 1. (continued)

<u>Sample</u>	<u>Acid added(%)</u>	<u>Acid present(%)</u>	<u>Total acid(%)</u>	<u>Acid found(%)</u>	<u>Std dev</u>
LP 1846 no.4	0.03	0.11	0.14	0.00*	
HACL	0.0	0.0	0.0	0.13**	
	0.0			0.11**	

Note: * Used 2.0 gm sample resulting in complete loss in recovery; all other samples are 0.5 grams.

** For impurity blank in ethanol. %HNO₃ is based on LP 1846.

Table 2. Aqueous titrations - nitric acid spiking study

<u>Sample</u>	<u>Sample wgt</u>	<u>Acid added</u>	<u>Acid present</u>	<u>Nitric acid actual total</u>	<u>Acid found</u>	<u>Std dev</u>
	(gm)	(%)	(%)	(%)	(%)	
DI H ₂ OI	1.0	0.0	0.00	0.00	0.01	
	1.0	0.00	0.00	0.00	0.01	
	1.0	0.065	0.065	0.065	0.069	
LP 1846 no.1	0.50	0.00			0.06	0.02
	0.47		---	---	0.07	
	0.49		---	---	0.06	
	0.99		---	---	0.02	
	1.03		---	---	***?	
	1.97		---	---	0.02	
	4.27		---	---	0.04	
	4.31		---	---	0.03	
	4.29		---	---	0.04	
	LP 1846 no.2	0.48	0.03	0.04	0.07	
0.49		0.03		0.07	0.07	
0.49		0.03		0.07	0.06	
0.50		0.065	0.04	0.10	0.09	
0.49		0.065		0.10	0.09	
0.49		0.065		0.10	0.11	
0.48		0.17	0.04	0.21	0.22	
0.48		0.29	0.04	0.33	0.31	
0.49		0.28		0.32	0.32	
0.49		0.33		0.37	0.35	

Table 2. (continued)

<u>Sample</u>	<u>Sample wgt</u>	<u>Acid added</u>	<u>Acid present</u>	<u>Nitric acid actual total</u>	<u>Acid found</u>	<u>Std dev</u>
	(gm)	(%)	(%)	(%)	(%)	
LP 1846 no.3	1.02	0.06	0.04	0.10	.**?	
LP 1846 no.4	4.26	0.004	0.04	0.04	.?	
	4.26	0.004		0.04	.?	
	4.23	0.03	0.04	0.07	.?	
	4.26	0.03		0.07	.?	
LP 1846 no.5	26.65*	0.00	0.04	0.04	.**?	
	28.53*	0.03		0.07	.**?	
	28.61*	0.00		0.04	0.03	
	28.53*	0.03		0.07	0.06	

Note: ? Nondiscernible end points using large samples.

* Total volume is 60ml. All others are 50ml.

** Determinations using S-curves.

Table 3. Nitric acid study - effect of diluent blank

<u>Diluent</u>	<u>Titration</u>	<u>Nitric acid</u>	
		<u>Present (%)</u>	<u>Found (%)</u>
Methanol HPLC Grade	Nonaqueous	0.00	0.01
Ethanol no.1 200 proof	Nonaqueous	0.00	0.01
Ethanol no.2 200 proof	Nonaqueous	0.00	0.12
DI water no. 1	Aqueous	0.00	0.01
DI water no. 2	Aqueous	0.00	0.03

Table 4. Comparison of aqueous versus nonaqueous titrations

<u>Sample</u>	<u>Aqueous (NaOH)</u>		<u>Nonaqueous (TBAH)</u>	
	<u>HAN (%)</u>	<u>TEAN (%)</u>	<u>HAN (%)</u>	<u>TEAN (%)</u>
LP-2	58.69	21.61	60.42	20.47
	58.67	21.00	60.45	20.42
	58.64	21.48	60.39	20.43
	58.61	21.46		
	58.65	21.76		
	58.65 ± 0.02	21.46 ± 0.19	60.42 ± 0.02	20.44 ± 0.02
LP-1846-01 (LP-3)	58.76	21.49	60.54	20.90
	58.85	21.51	60.60	20.95
	58.81	21.76	60.64	20.82
	58.71	22.18		
	58.84	22.35		
	58.70	21.75		
	58.78 ± 0.06	22.01 ± 0.33	60.59 ± 0.04	20.89 ± 0.05

Note: 1. All values are corrected for free nitric acid and ammonium nitrate.

2. LP-2 is lot ABY87FS2CO13

Table 5. Comparison of aqueous and nonaqueous synthetic LP 1846 HAcI/TEAcI titrations

Titration Type	Diluent	Acetone (%)	Reaction time (min)	Titrant volume, mls	
				HAcI	TEAcI
Nonaqueous	Ethanol	1.0	0.0	14.91	17.28
				<u>14.87</u>	<u>17.23</u>
				±0.02	±0.025
		5.0	0.0	14.95	17.33
				<u>14.93</u>	<u>17.31</u>
				±0.01	±0.01
		10.0	0.0	14.93	17.32
				<u>14.87</u>	<u>17.26</u>
				±0.03	±0.03
Actual Concentration Experimental		<u>10.0</u>	<u>15.0</u>	<u>14.89</u>	<u>17.26</u>
			60.8% HAN 61.4% HAN	19.2% TEAN 21.6% TEAN	
Aqueous	Water	1.0	0.0	17.19	20.13
				<u>17.14</u>	<u>20.06</u>
				±0.025	±0.035
		5.0	0.0	17.11	20.03
				<u>17.20</u>	<u>20.10</u>
				±0.045	±0.035
		10.0	0.0	17.14	20.03
				<u>17.15</u>	<u>20.02</u>
				±0.005	±0.005
Actual concentration Experimental		<u>10.0</u>	<u>15.0</u>	<u>17.14</u>	<u>20.04</u>
			60.8% HAN 58.5% HAN	19.2% TEAN 21.9% TEAN	

Note: High purity hydroxylammonium hydrochloride and triethanolammonium hydrochloride was used to prepare solutions containing the same amount of cations (hydroxylamine or triethanolamine) which would be present in the nitrate solutions of LP 1846.

Table 6. Metals analysis of two lots of LP 1846 by ICP

<u>Metal</u>	<u>LP-2,</u> ppm	<u>LP-3,</u> ppm
Iron	<0.09	2.06 (polarography:0.31ppmFe ⁺³)
Chromium	0.74	0.40
Copper	<0.18	<0.17
Nickel	0.88	0.34
Cobalt	<0.09	<0.09
Lead<0.87	<0.87	
Tin	3.06	3.03

Note: The difference between polarography and ICP illustrates that the FE⁺³ in the LP is complexed and not available as Fe⁺³.

Table 7. Comparison of graphite furnace AA and ICP metals analyses of LP 1845 lot 1845-01-02

<u>Metal</u>	<u>ICP (ES)/(IS) and GPA</u>		<u>GPAA</u>	<u>ICP</u>
	<u>Perkin Elmer (ref 12)</u> (ppm)	<u>ARL (ref 13)</u> (ES)	<u>Det limit</u> (ppb)	<u>Det limit</u> (ppb)
Al		<0.075	0.04	12
Cu	0.11(ES)	<0.020	0.02	8
Cu	0.24(IS)			
Cr	0.02(ES)	<0.010	0.01	5
Cr	0.03(IS)			
Ni	0.00(ES)	<0.020	0.10	20
Ni	0.04(IS)			
Fe	0.87(ES)	1.0	0.02	16
Fe	1.76(IS)			
Fe	1.87(GPAA)			

Note: IS = internal standard technique. Scandium used as IS
 ES = external standard technique (no internal standard)
 GPAA = graphite furnace AA
 Dilution : GPAA = 1/100, PE ICP = 0, ARL ICP = 1/9th
 Same results obtained for lot 292

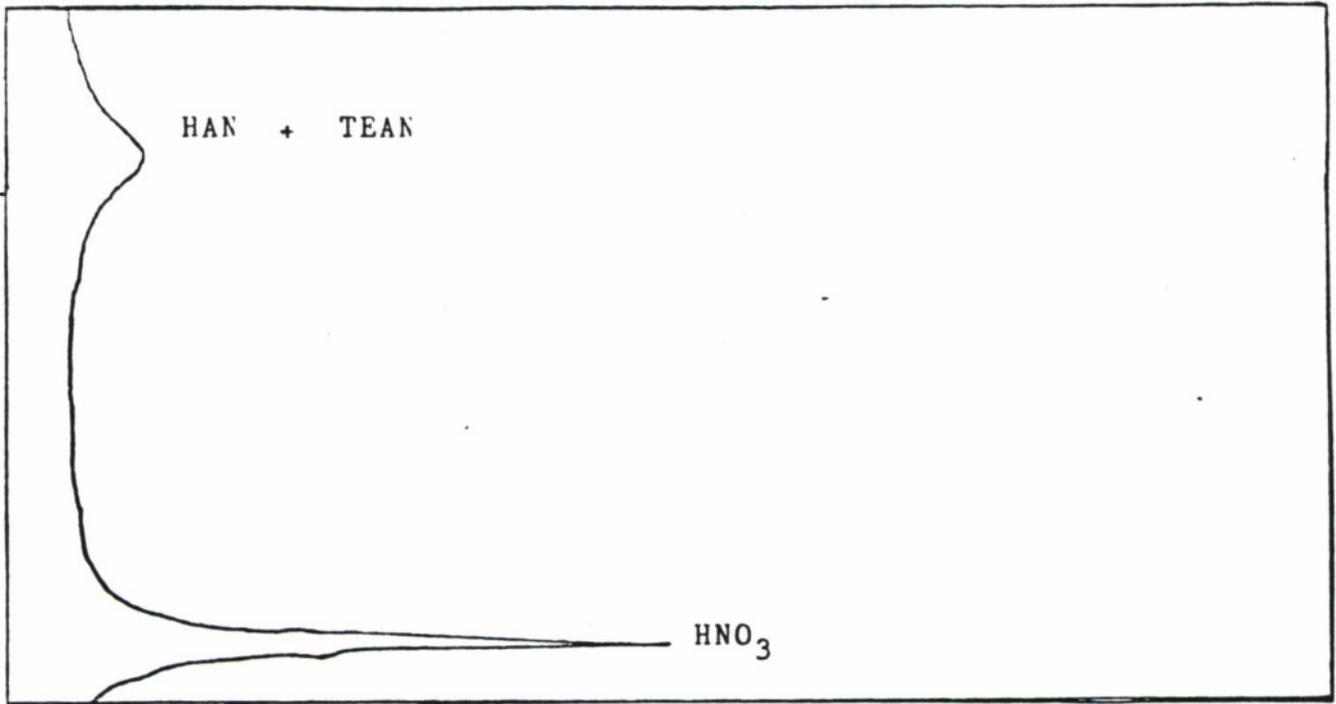


Figure 1. Effect of ketone in solvent on titration of acid

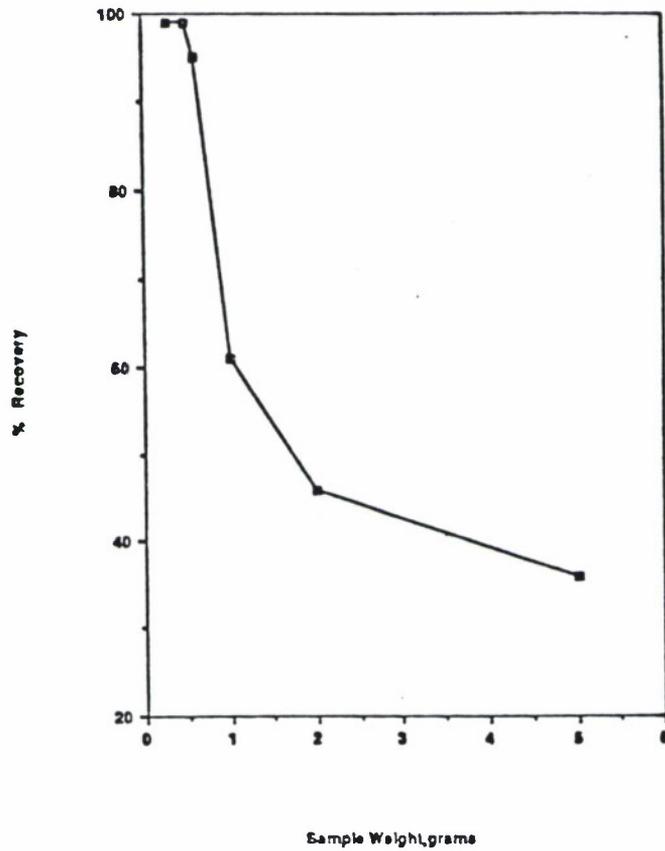
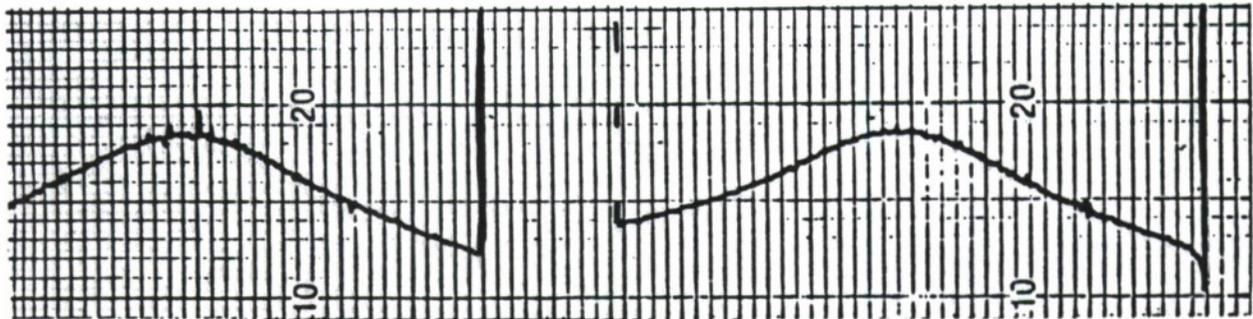
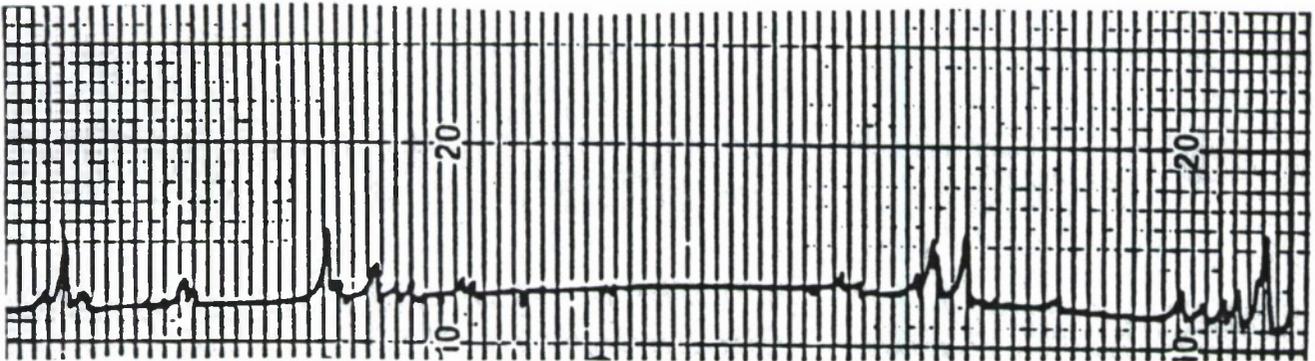


Figure 2. Nitric acid titration - percent recovery versus sample weight



0.5gms LP 1846-03-08 + 255 μ l 0.0103N HNO₃ in 50ml Ethanol
Titrant 0.0095N TBAH

Figure 3. Nonaqueous titration derivative curves with optimized sample size



2.0082gms LP 1846-03-08 + 1.0ml 0.0103N HNO₃ in 50ml Ethanol

Figure 4. Nonaqueous titration derivative curve with concentrated sample

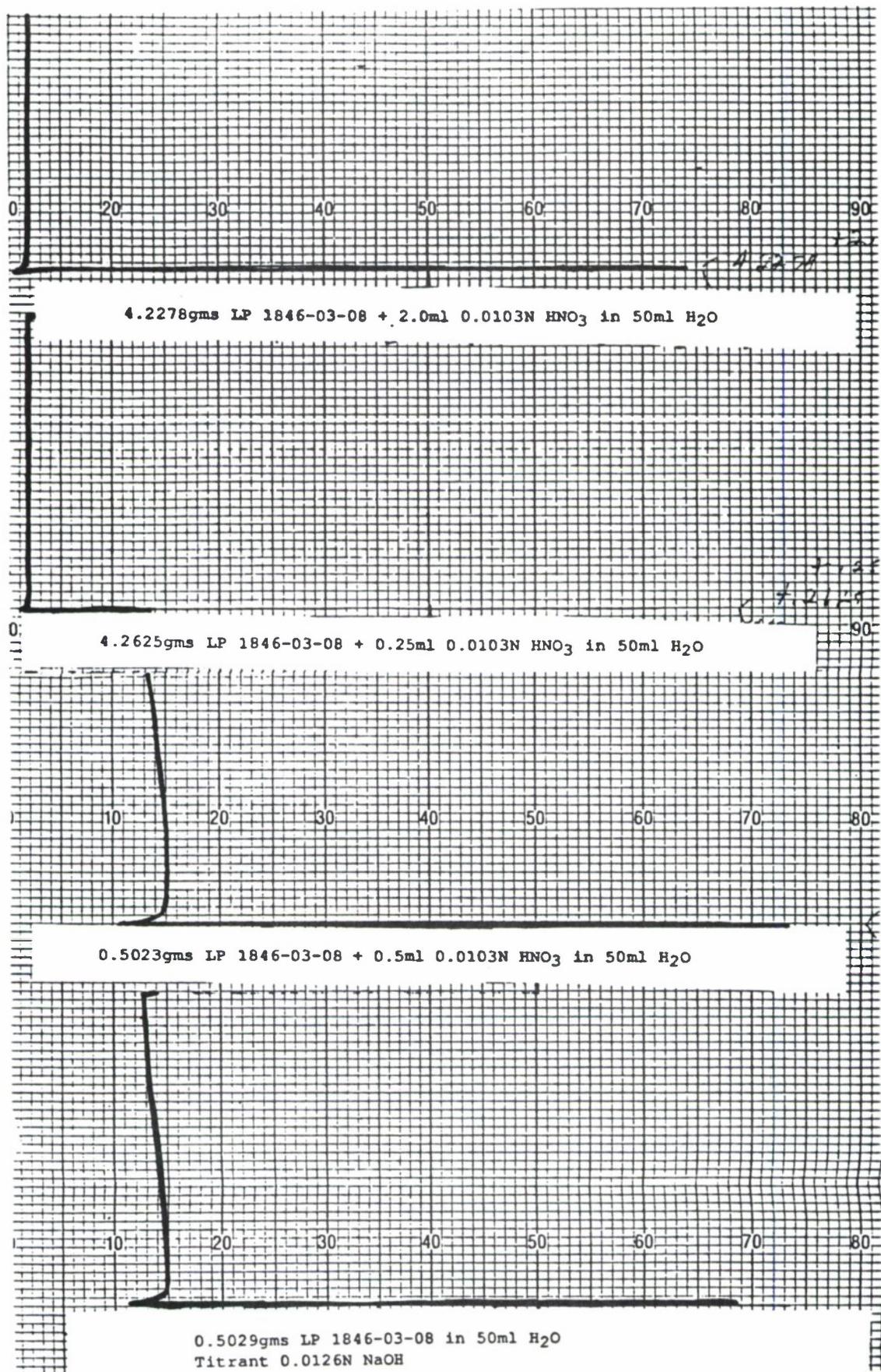
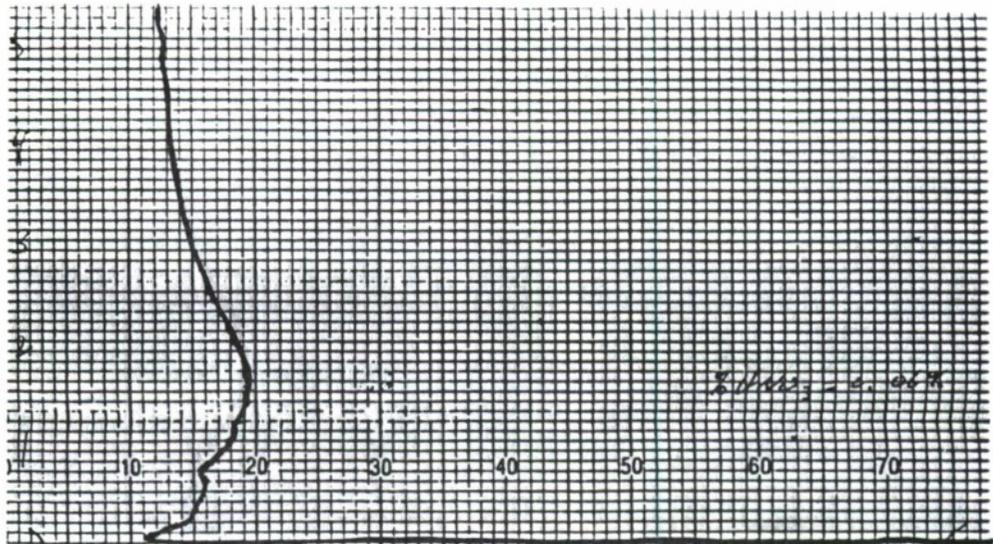
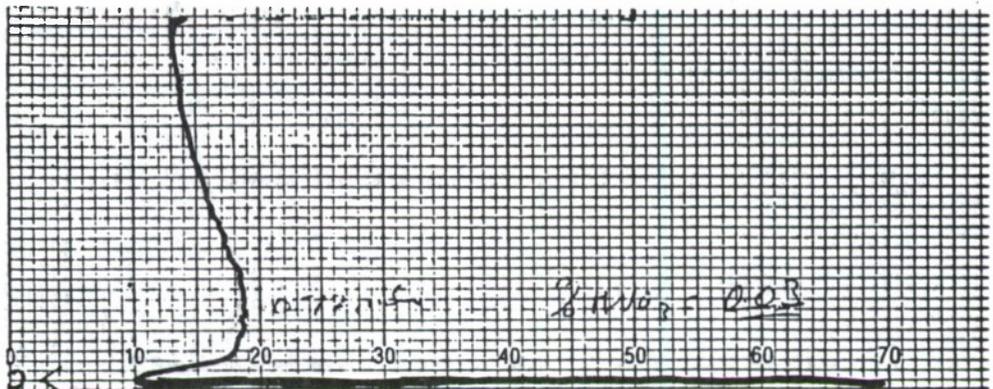


Figure 5. Effect of sample concentration in aqueous titration derivative curves



28.5340gms LP 1846-03-11 + 15ml 0.0103N HNO₃ + 25ml H₂O



28.6135gms LP 1846-03-11 + 40ml H₂O
 Titrant 0.178N NaOH

Figure 6. Aqueous titration derivative curves

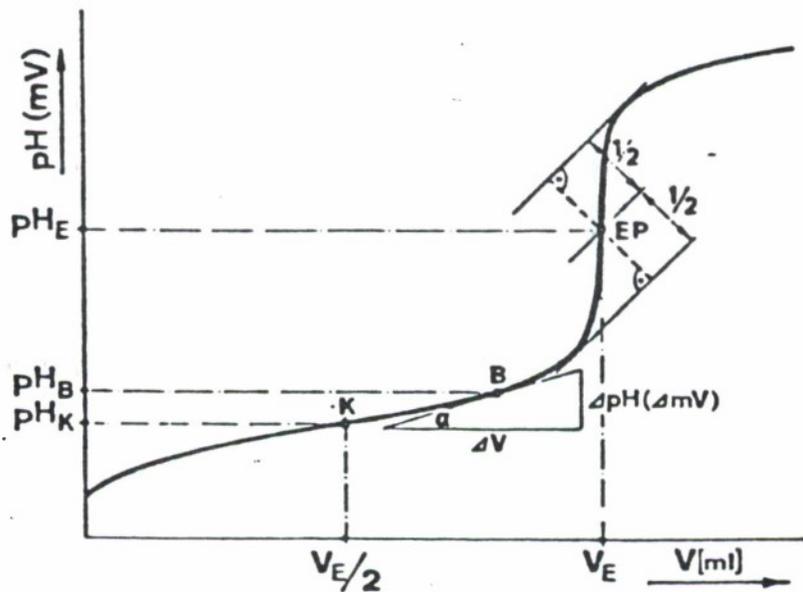


Figure 7. Potentiometric titration S-curve

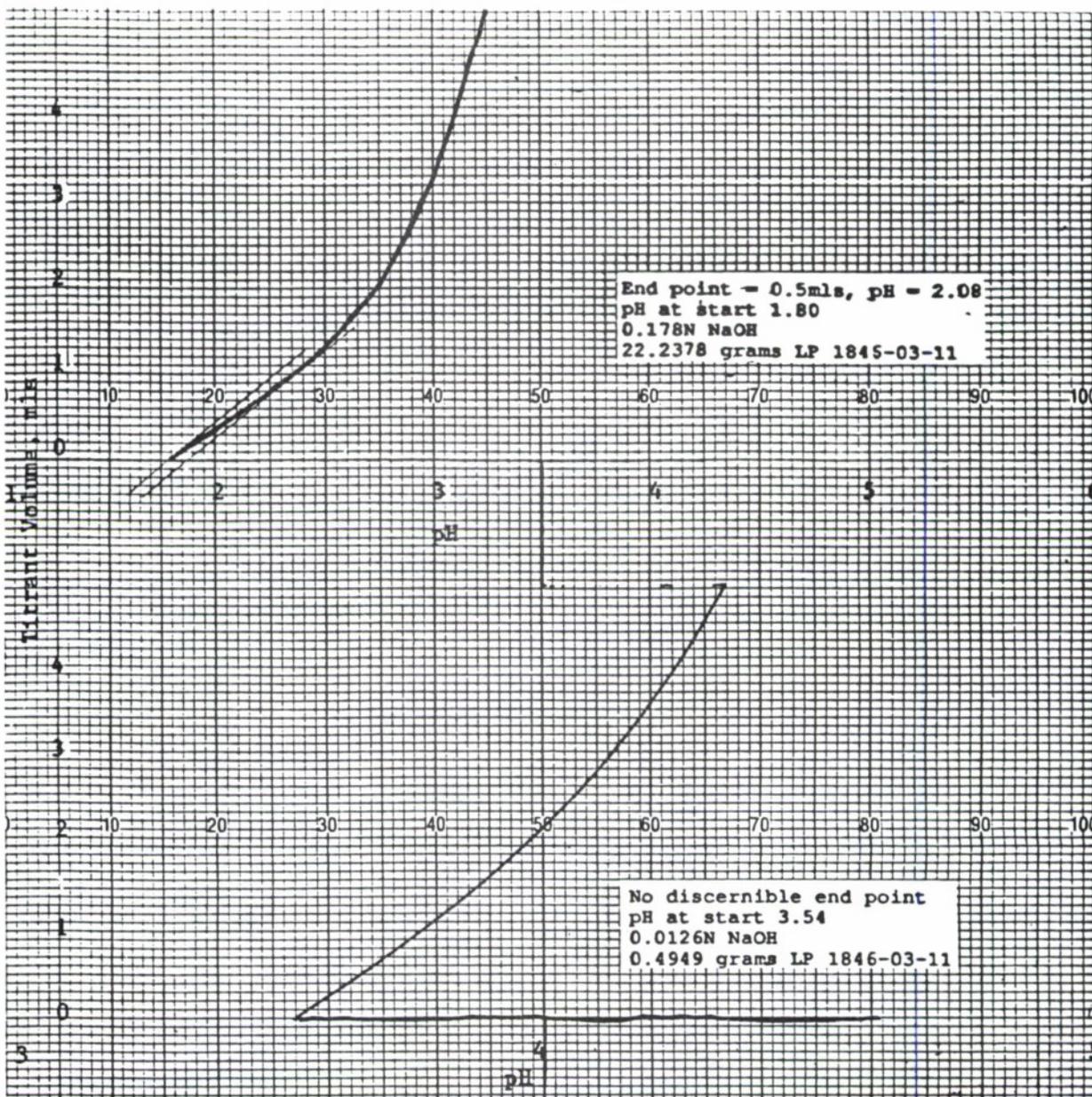


Figure 8. Aqueous titration S-curves for nitric acid

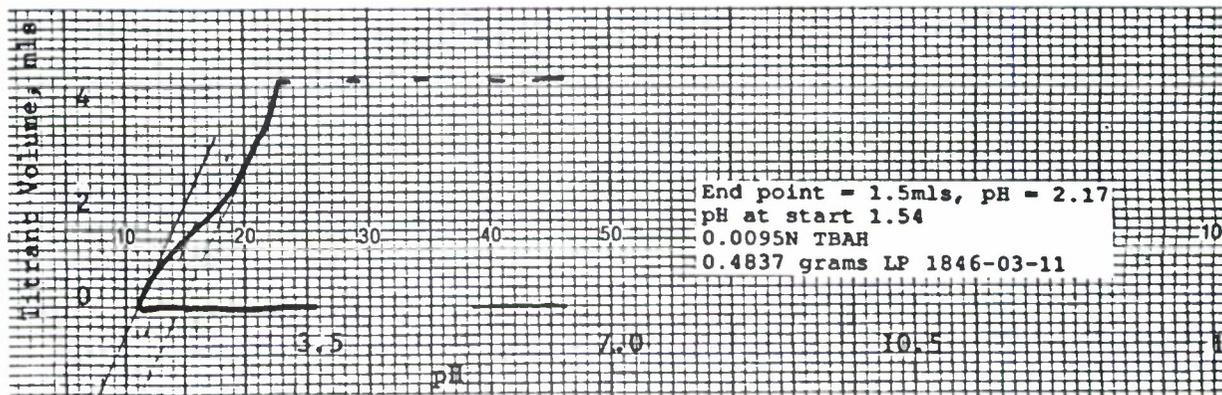


Figure 9. Nonaqueous titration S-curves for nitric acid

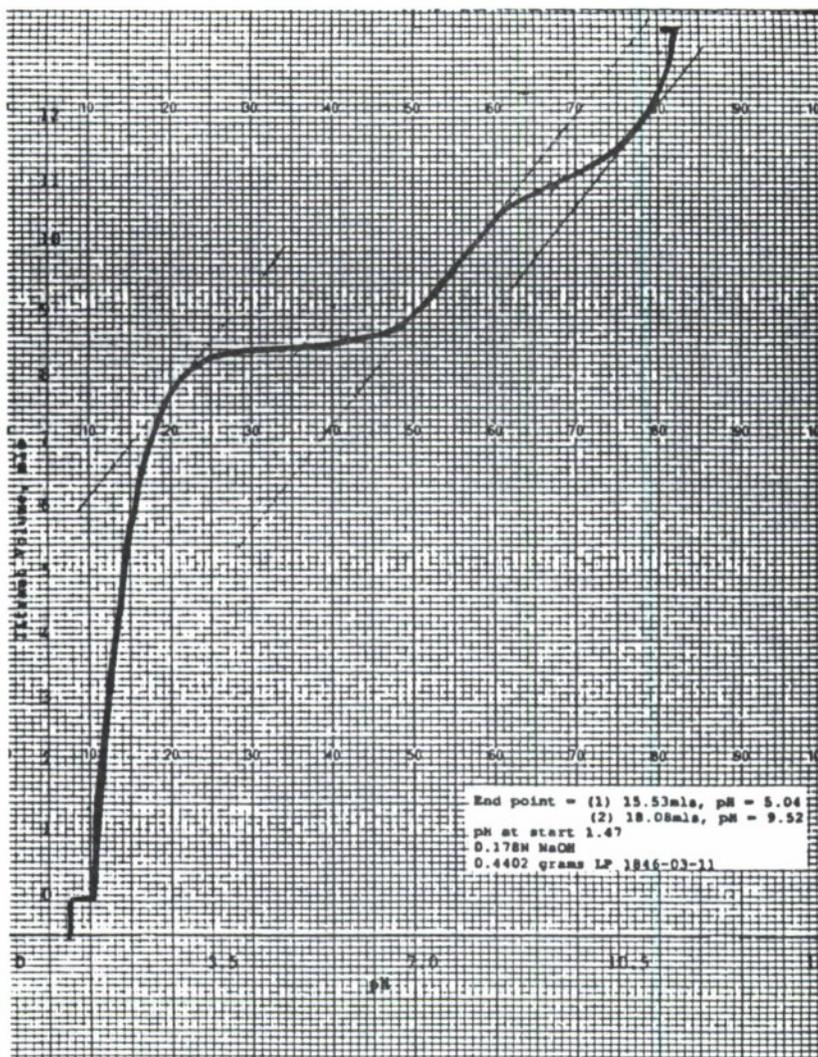


Figure 10. Aqueous titration S-curve for HAN/TEAN

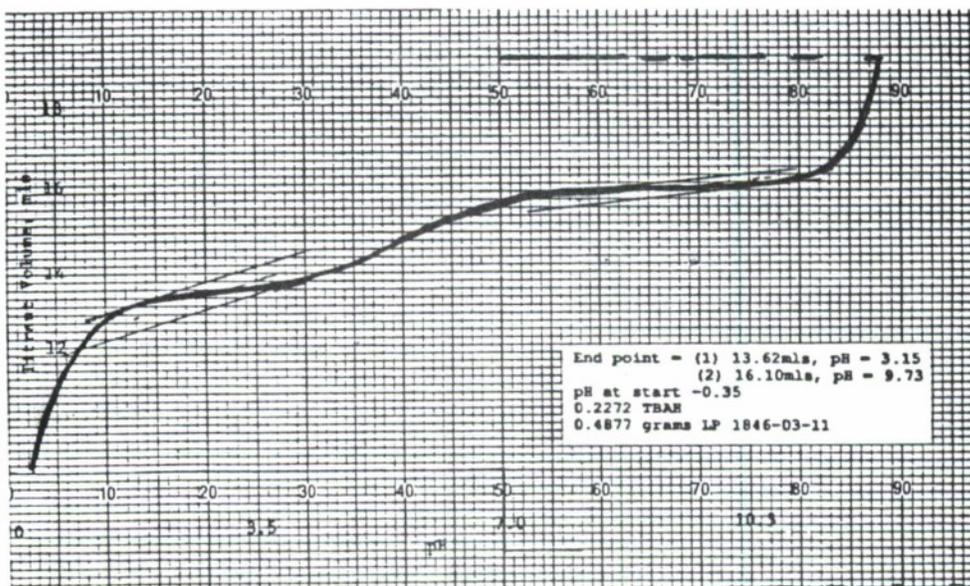
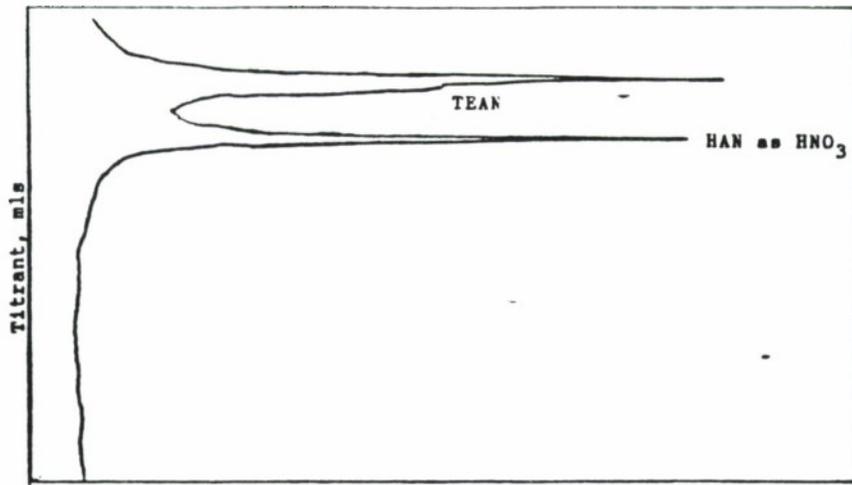
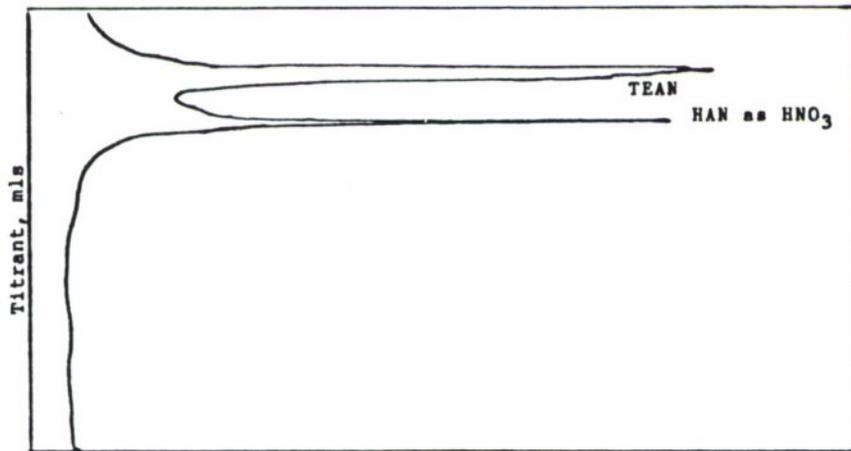


Figure 11. Nonaqueous titration S-curve for HAN/TEAN



LP + Ammonium Nitrate



LP Only

Figure 12. Comparison of liquid propellant titration curves for impurities

Ethanolamine Analysis
 IC-Pak TM; 4mM HNO₃ / 5% MeOH at 2 ml/min; BP=2000psi
 Conductivity Detection; BC=1230uS

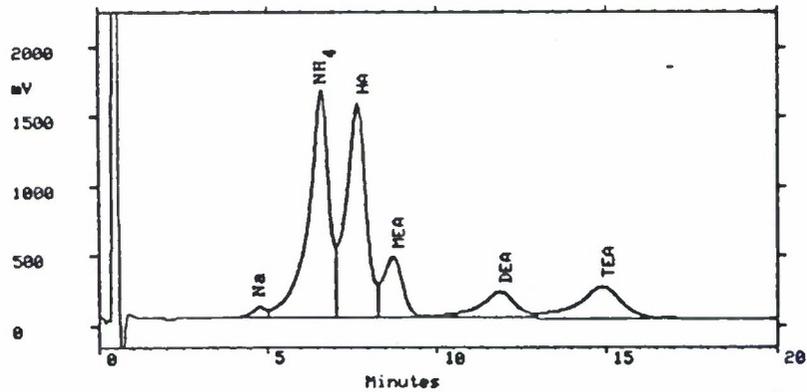


Figure 13. Chromatogram of cation standards

Extraction Condition:

400 atm, 65°C for 15 min.
CO₂ + 0.3% formic acid
100 mg on celite

Chromatography Conditions:

CO₂ + 0.3% formic acid
100 atm → 485 20 atm/min
100°C
10 cm x 1.0 mm I.D. 5 um
Methyl Deltabond

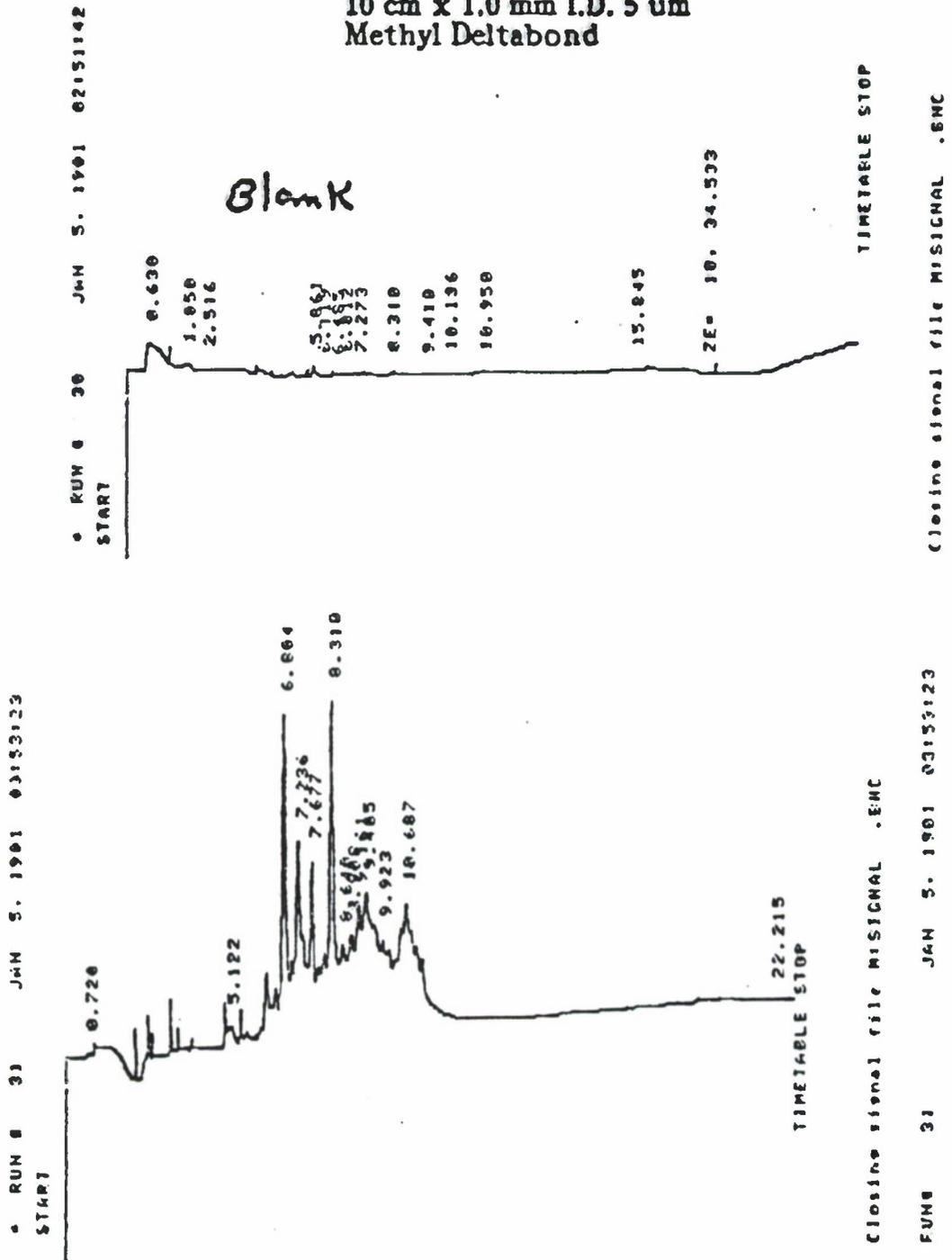
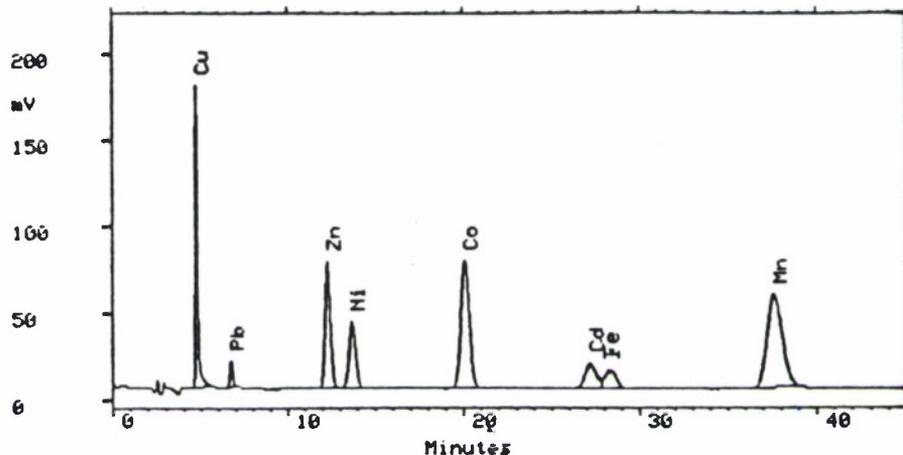


Figure 14. Supercritical fluid chromatograms of liquid propellants

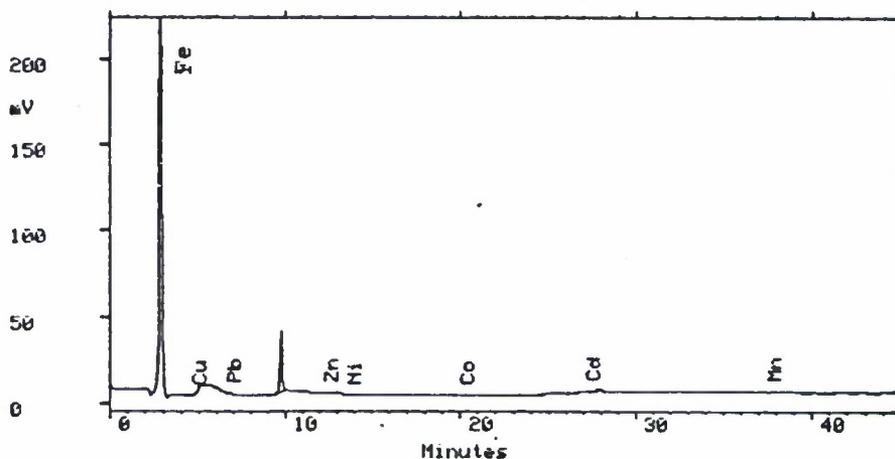
Transition Metal Method; uBondapak C18
 2mM NaDS / 50mM Tartaric Acid pH=3.4 with NaOH
 Post Column PAR Detection at 520nm

Chromatogram of TMSTD



Peak Name	Ret time	Area	Height	Type	Response	Amount
Cu	4.71	1758708	183794	BB	1.75871e+06	0.5 ppm
Pb	6.69	212112	15542	BB	2.12112e+05	1.0
Zn	12.27	1622314	73563	EV	1.62231e+06	0.5
Ni	13.66	1049294	38397	VB	1.04929e+06	1.0
Co	20.05	2543774	73778	BB	2.54377e+06	0.5
Cd	27.17	621232	13672	BV	6.21232e+05	1.0
Fe	28.36	451159	9671	VB	0.00000e+00	
Mn	37.55	3169191	53214	BB	3.16919e+06	1.0

Chromatogram of LP1TM



Peak Name	Ret time	Area	Height	Type	Amount
UNL.DOWN	9.76	315111	37405	BB	0.000

Figure 15. Chromatogram of transitions metals standard and transition metals in liquid propellant

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GLOSSARY

AA	Atomic absorption
AN	Ammonium nitrate
ARL	Army research lab
DEAN	Diethanolammonium nitrate
EAN	Ethanolammonium nitrate
ES	External standard
GPAA	Graphite furnace atomic absorption spectrophotometry
HACL	Hydroxylammonium chloride
HAN	Hydroxylammonium nitrate
IC	Ion chromatography
ICP	Inductively coupled plasma spectrophotometry
ICP/MS	Inductively coupled plasma spectrophotometry/mass spectrometry
IS	Internal standard
PAR	Post column reactant
SFC	Supercritical fluid chromatography
TBAH	Tetrabutyl ammonium hydroxide
TEAN	triethanolammonium nitrate
TEACL	Triethanolammonium chloride
UV	Ultra violet

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