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DEVELOPMENT OF AQUEOUS AND NONAQUEOUS TITRIMETRIC METHODS FOR LIQUID PROPELLANTS

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Armament Engineering Directorate
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The U.S. Army has made a commitment to develop liquid gun propellants as a potential replacement of solid propellants used in various gun systems. In order to monitor the propellants during storage, a study was conducted to develop analytical capabilities for this purpose. The storability of liquid propellants is required to determine whether there is any instability, its cause, and if necessary, its prevention. Titrimetry was selected to monitor two of the species present which were most illustrative of propellant conditions and critical to performance. In the course of this study, the merits of aqueous and nonaqueous techniques were discovered. As a result of this study, a capability is availaible to monitor some of the vital components and contaminants in liquid propellants during storage.

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INTRODUCTION

The U.S. Army has been engaged in the search for intensive munitions for guns in tanks and self-propelled howitzers. Liquid Propellants have been categorized as an intensive munition (ref 1) and are presently under consideration as a potential replacement of solid propellants. The logistical, ballistic, and cost savings feature propellant prompted an extensive program for their characterizations. The integrity of these propellants, after being stored for extended periods of time, is required to assure that the ballistic parameters are met. In order to establish these criteria, long-term storage studies of liquid propellants are required to determine their stability and storability.

The use of liquid propellants as a replacement for solid propellants in diverse gun applications necessitates extensive characterization of the propellant system. This requirement has resulted in the necessity to develop analytical techniques that will establish the capability to monitor the composition of liquid propellants during storage. Some of the important features which were considered for candidate techniques included reproducibility, reliability, simplicity, safety, and environmental impact.

The propellant systems currently under investigation are stoichiometric mixtures of hydroxylammonium nitrate (HAN) with an alkyl ammonium nitrate in water. The alkylammonium nitrate which is being considered at present is triethanolammonium nitrate (TEAN). A typical composition called LP 1846 has 61% HAN, 19% TEAN, and 20% water. The molar ratio of this mixture is 7:1 for HAN to TEAN which is stoichiometric for conversion to the desirable products of combustion of carbon dioxide, water, and nitrogen.

The knowledge of the aging effects of the basic liquid propellant constituents and stability when exposed to contaminants during long-term storage is essential. This information is critical since any significant deviation in the basic propellant formulation will result in a loss in ballistic performance and propellant lifetime as well as causing potential safety problems. Therefore, it is necessary to determine the effects of temperature and contaminants on the stability of liquid propellants and provide analytical techniques to monitor the gas and liquid phase compositions before and after exposure.

Analyses are required to both identify and quantify major propellants, contaminants, and degradation products in order to provide a basis for desired criteria. Low level concentrations of contaminants or impurities which have been detailed previously (ref 2 and 3) such as ammonium nitrate (AN), nitric acid, morpholines, hydrazines, nitrosoamines, nitrogen oxides, nitrogen, and trace amounts of transition metal ions can be expected to be found.

EXPERIMENTAL

Chemicals

LP 1846 propellant was prepared by Thiokol Chemical Corp., Elkton, MD and supplied by BRL, Aberdeen, MD.

The hydrochloride derivates of HAN and TEAN were purchased from Aldrich Chemical Co., Milwaukee, WI.

The high purity solvents and regeants are commercial products. Ethanol (Pharmco, NJ). sodium hydroxide, methanol, and acetone (Fisher, NJ).

The tetrabutylammonium hydroxide is a commercially avaliable titrant in menthanol (Aldrich Chem Co.).

Titrators

The potentiometric titrations were carried out on a Metrohm potentiograph Model E-536 and a Model 655 Metrohm Dosimat.

RESULTS

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 provided some difficulty. In-depth investigations of the use of titrimetry as well as alternative techniques such as ion chromatography (IC) and supercritical fluid chromatography (SFC) 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). Methyl isobutyl ketone was used in this method to convert HAN to a stronger acidic product, nitric acid. TEAN, 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, a very weak acid ($Kb < 10^{-12}$) which is not titrated.

$$\underset{\text{HAN}}{H_3NOHNO_3} + R_2C{=}0 \text{--->} \underset{\text{Oxime}}{R_2C{=}NOH} + HNO_3 = H_20 \qquad (1)$$

HAN based liquid propellants can undergo decomposition as a result of the presence of various contaminants such as nitric acid and transition metals with formation of numerous products some of which are shown in equation 2:

$$aH_3NOHNO_3 \dashrightarrow bHNO_3 + cN_xO_y + dN_2 + eH_2O + fNH_4NO_3 + Z \tag{2}$$

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 differentiate free nitric acid separate from nitric acid produced from keytone/HAN reaction. This was accomplished by performing two titrations. The keytone was eliminated from the sample solvent permitting the HAN to remain unchanged. The free nitric acid from HAN to remain unchanged. The free nitric acid from HAN decomposition or propellant production could then be titrated. This is impossible since the HAN and TEAN which are very weak acids from one break in the titration curve after the stronger, free nitric acid break. Tetrabutylammonium hydroxide of 0.01N in methanol was used as the titrant with 50 ml of ethanol as the sample solvent. In order to provide the necessary accuracy for concentrations of HNO_3 <0.5%, an 0.6-gram sample was chosen; and for concentrations of HNO_3 >0.5%, an 0.3-gram sample was required (refs 2 and 3). Finally, the HAN/TEAN could be determined in a seperate titration with addition of keytone 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 the aqueous was >±0. 02 and for the nonaqueous <±0. 02 (tables 1 and 2). The titration curves for the nonaqueous method were more sensitive. The choice of sample weight was also critical. In keeping with acceptable titration techniques 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 1 where percent recovery is dramatically reduced as sample concentration is increased. The calculations for figure 1 were made without subtraction of the solvent blank in order to show the effect of large samples. The actual recovery of nitric acid added (table1) is a complete loss or zero recovery with sample sizes greater than one gram

The choice of methods for this study was restricted by sample quantities available, safety regulations, directives to reduce waste and sample usage, and analytical methods had to be tailored to comply with these restrictions.

The original HAN/TEAN method by Kasler produced titration curves which produced breaks that were not sufficiently discernible for the accuracy required for this program. In this study, first derivative curves were used to provide more easily defined end points. Acetone was substituted for the higher keytones used by other investigators (refs 3 and 4) for conversion of HAN to nitric acid which led to smoother and better defined titration curves. Pre-addition of titrant was used to reduce analysis time and provide accurate data. The sample size (0.6 g) was within accepted levels for ionic strengths of less than 0.1 (eqs 5 through 7), but sufficient for the desired accuracy and precision. Several titrants were tested, and tetrabutyl ammonium hydroxide (TBAH) was found to be applicable to both nitric acid and HAN/TEAN analyses. The prefered titrant for free nitric acid from degradation and production was n-butylamine in methanol, but the use of both titrants was not pursued. 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 g with pre-addition of 15.0 ml of titrant in 50 ml of ethanol/acetone (100:1) (refs 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 3. Calculation of the blank as nitric acid shows that a significant error would be introduced in the case of ethanol 2.

The aqueous system was compared to nonaqueous titration of two liquid propellant lots (table 4) and of synthetic lot using hydrochloride standards (table 5). Both LP-2 and LP-3 were specification grade mixtures containing 60.8$\pm$ 0.5% HAN. As a result, the data in table 4 indicate that the nonaqueous titration provides more realistic results. This is also confirmed with the data in table 5. In this case, pure hydrochloride standards were used to prepare solutions containing the same amount of cation (hydroxlyamine 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 only interesting observation in the TEAN comparison is that the aqueous titration results in higher TEAN (TEAC1) concentrations. This may be due to unreacted HAN (HAC1) which would account for low HAN values. If the effect of molecular weight from equation 3 is considered, 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 (eq 3). For example, a weight of 80 versus TEAN with a molecular weight of 212 would effectively increase the TEAN concentration detected due to its presence by more than twice the amount.

$$\%X = \frac{(100)\,[(\text{mls titrant})\ (\text{N titrant})\ (\text{MW}/1000)]}{\text{Sample weight, grams}} \qquad (3)$$

In order to provide an analytical capability, an overall review and understanding of the basic principals 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 nor 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 weak acidic species such as TEAN. That is, the amplitude of the derivative curve is greater and much sharper. By careful observance of titrant and solvent effects and the increased sensitivity of nonaqueous media, it was possible to qualitatively and semiqualitatively distinguish between weakly acidic species, TEAN an AN. This characteristic has been observed by others in ethanol and other nonaqueous media (ref 6).

To be consistent with general practices set forth by numerous investigators, a dilute system was considered as an optimum approach with ionic strengths less than 0.1 (ref 7). These criteria are fulfilled by both nonaqueous methods which were developed (eqs 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. 1). Since buffering capacity is the property of a solution to resist pH change, it is requisite to reduce buffering power through dilution especially in analyses which require monitoring traces or slight changes. Evidence of buffering as a result of concentrated samples is illustrated in the derivative curves of figures 2 through 5. A standard symmetrical nonaqueous titration is shown in figure 2; the effect of a larger sample in which the curve becomes very noisy and shallow in figure 3; and the effect of increasing sample size using the aqueous method whose curves are asymmetrical in figure 4. As sample size was increased, the curve became increasingly shallow and eventually indiscernible. Figure 5 is an aqueous titration with a very large sample (~30 grams) in which the curve is measurable but very noisy and asymmetrical. 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:

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

where Aa andAb are activities (~ concentrations).

Since Aa = Ab is approximately fulfilled by $V_E/2$, the point K on the curve can be easily determined resulting in the appropriate pHk form which the corresponding pKa can be found (fig. 6). Although the pKa determined in this manner is not exact, it is sufficient for this comparision. 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 titration techniques currently being employed for HAN-based propellants (figs. 7 through 10). Calculations are shown below for several of the aqueous and nonaqueous titration S-curves of LP 1846-03-11 from figures 7 through 10:

	End point						Start
Method	ml	pH	b	pK	%HNO_3	%HAN	pH
Aqueous	0.50	2.08	0.28	1.92	0.03		1.80
Nonaqueous	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
Nonaqueous	13.62	13.15	0.44	~0.3		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 buffing capacity which would make the aqueous method more susceptible to error. This larger buffering capacity is the function of the larger sample size, 20 to 30 grams versus the smaller sample for nonaqueous method (0.5 g) .

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 8.94 M and TEAN at 1.34 M are as follows:

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

HAN = ml [M/ (1000 ml/L) = 0.00375 moles

TEAN = 0.00056 moles (5)

Diluted in 50 ml,

HAN = [(moles x 1000 ml/L) /ml] = 0.074 M (6)

TEAN = 0.011 M

Ionic strength, μ,

$$\mu = 1/2\ \Sigma\ \mu z^2 = 0.085 \qquad (7)$$

In the concentrated systems, the curves are more asymmetrical (figs. 2 through 10) 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 solution, HA, the equilibrium is determined by the magnitude of the ionization constant:

$$[H^+]\,[A^-] \,/\, [\,HA] = Ka \tag{8}$$

and

$$[H^+] = \{\,[\,HA] \,/\, [A^-]\,\} \times Ka$$

If a mixture of a weak acid and its salt (KA) is considered, 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 all of the acid present can be considered to be in the undissociated form (ref 8).

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. Since these contaminants could have a large impact on the TEAN determination, an alternative method for TEAN is necessary. Due to the observed limitations of titrimetry, ion and supercritical fluid chromatography are being investigated for the analysis of HAN, TEAN, EAN, DEAN, and AN. This does not preclude the use of titrimetry. Potentiometric titrimetry appears 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 used until such time that either IC or SFC or both are optimized. Both IC and SFC instrument manufacturers * were consulted on the above-mentioned analyses which has resulted in feasible approaches for further investigation. One of the important considerations which led to SFC was environmental impact and waste disposal.

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* J. Krol, Waters Division of Millipore, 1988
M. Ashraf-Khorassani of Suprex Corporation, 1989

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 conductivity detector were used for the separation and detection. A 20 to 100 µl size sample of diluted liquid propellant (3/5000 in water) was injected using 1 to 4 mm HNO_3/0-15% methanol as the eluant. The separation using this technique resolves all the above-mentioned species (refs 2 and 3). The nitric acid molarity effects the speed of elution of the HAN and AN primarily and this methanol concentration, primarily the TEAN. This combination can be used to vary the elution times of the components of interests 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 has been shown to provide the desired results and merits further investigation. The chromatographic column used in this separation for all the species of interest was 10 cm x 1.0 mm x 5 µm 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 (ref 10).

CONCLUSIONS

The final selection of analytical techniques for this program is still under investigation. The uses of titrimetry have been illustrated as well as the advantages of chromatography. The development of the later has far-reaching utility and applicability to many facets of this program. 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 the particular requirements. This investigation has endeavored to provide some incite into their advantages and disadvantages.

Table 1. Determination of nitric acid in spiked propellant samples by nonaqueous titration

Sample	%Acid added	%Acid present	Total % acid	% Acid found
Ethanol	0.03	0.0	0.03	0.02
	0.03		0.03	0.02
	0.05		0.05	0.04
	0.05		0.05	0.04
	0.13		0.13	0.12
	0.13		0.13	0.12
LP 1846 No.1	0.0	0.08	0.08	0.09
	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
	0.0			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
				0.09
				0.11
				0.11
	0.03		0.13	0.13
				0.13
				0.13
				0.12
	0.07		0.17	0.17
				0.16
				0.17
				0.16
LP 1846 No. 4	0.03	0.11	0.14	0.00*

Used 2.0 g sample resulting in complete loss in recovery; all other samples are 0.5 g.

Table 2. Determination of nitric acid in spiked propellant samples by aqueous titrations

Sample	Sample wgt,g	% Acid added	%Acid present	% Nitric acid actual total	%Acid found
DI H2O	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
	0.47		--	--	0.07
	0.49		--	--	0.06
	0.99		--	--	0.02
	1.03				[a,b]
	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	0.05
	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
	0.50	0.065	0.04	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
	0.48	0.28		0.32	0.32
	0.49	0.33		0.37	0.35
LP 1846 No. 3	1.02	0.06	0.04	0.10	[a,b]
LP 1846 No. 4	4.26	0.004	0.04	0.04	[b]
	4.26	0.004		0.04	[b]
	4.23	0.03	0.04	0.07	[b]
LP 1846 No. 5	28.65[c]	0.00	0.04	0.04	[a,b]
	28.53[c]	0.03		0.07	[a,b]
	28.61[c]	0.00		0.04	0.03
	28.53[c]	0.03		0.07	0.06

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[a] Nondiscernible end points using large samples.

[b] Determinations using S- curves.

[c] Total volume is 60 ml; all others are 50 ml.

Table 3. Effect of diluent blank in nitric acid study

Diluent	Titration	Nitric acid Present	Nitric acid Found
Methanol HPLC grade	Nonaqueous	0.00	0.01
Ethanol 1 200 proof	Nonaqueous	0.00	0.01
Ethanol 2 200 proof	Nonaqueous	0.00	0.12
DI water 1	Aqueous	0.00	0.01
DI water 2	Aqueous	0.00	0.03

Table 4. Comparison of aqueous versus nonaqueous titrations for HAN and TEAN

Sample	Aqueous (NaOH) % HAN	Aqueous (NaOH) % TEAN	Nonaqueous (TBAH) HAN	Nonaqueous (TBAH) % TEAN
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 ABY87FS2C013.

Table 5. Comparison of aqueous and non aqueous synthetic 1846 HACL/TEACL titrations

Titration type	Diluent	Percent acetone	Reaction time, min	Titrant HA · CL	Volume, mls TEA · CL
Nonaqueous	Ethanol	1.0	0.0	14.91	17.28
				14.87	17.23
				±0.02	±0.025
		5.0	0.0	14.95	17.33
				14.93	17.31
				±0.03	±0.01
		10.0	0.0	14.93	17.32
				14.87	17.26
				±0.03	±0.03
		10.0	15.0	14.89	17.26
	Actual concentration		60.8% HAN	19.2% TEAN	
	Experimental		61.4% HAN	21.6% TEAN	
Aqueous Water		1.0	0.0	17.19	20.13
				17.14	20.06
				±0.025	±0.035
		5.0	0.0	17.11	20.03
				17.20	20.10
				±0.045	±0.035
		10.0	0.0	17.14	20.03
				17.15	20.02
				±0.005	±0.005
		10.0	15.0	17.14	20.04
	Actual concentration		60.8% HAN	19.2% TEAN	
	Experimental		58.5% HAN	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.

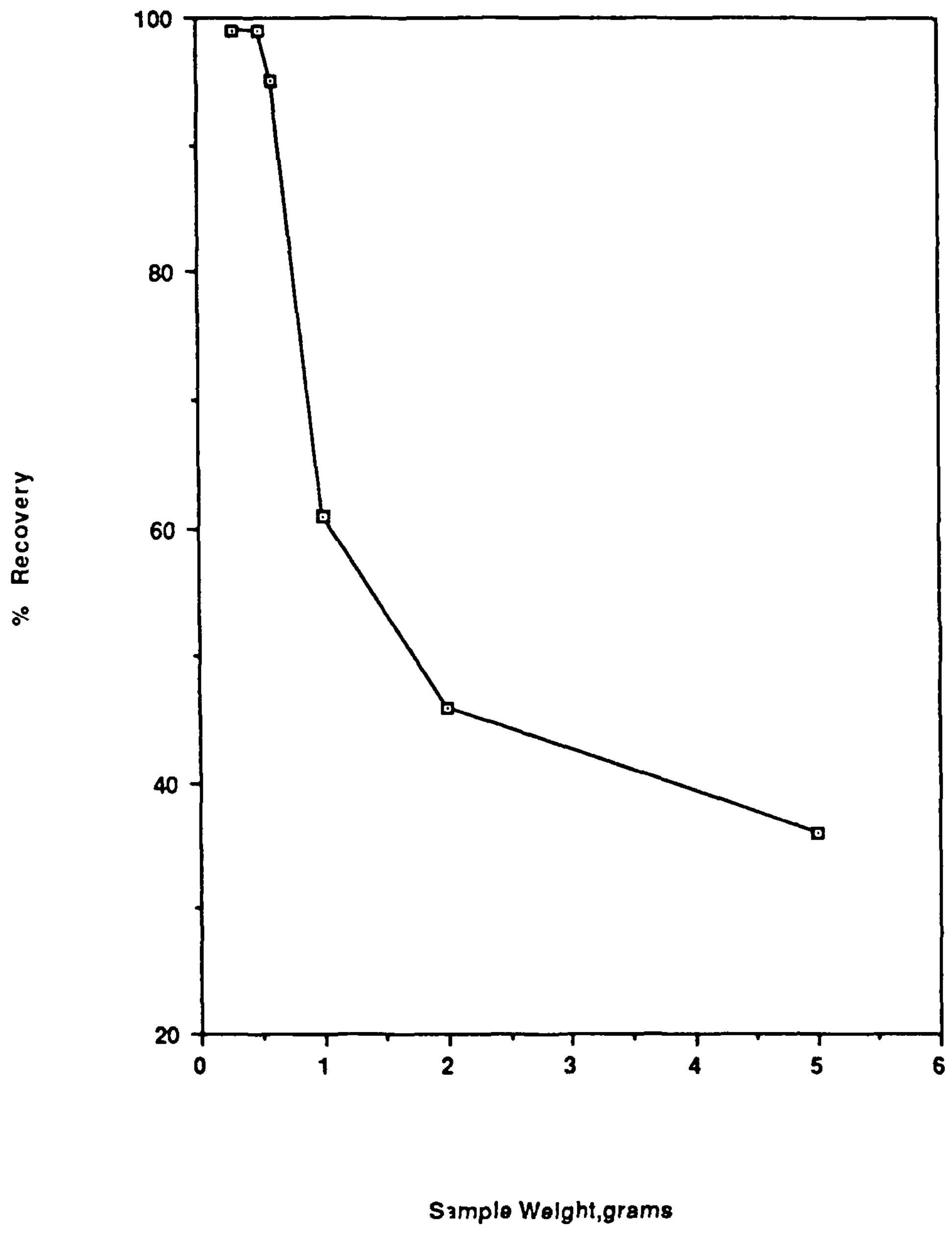
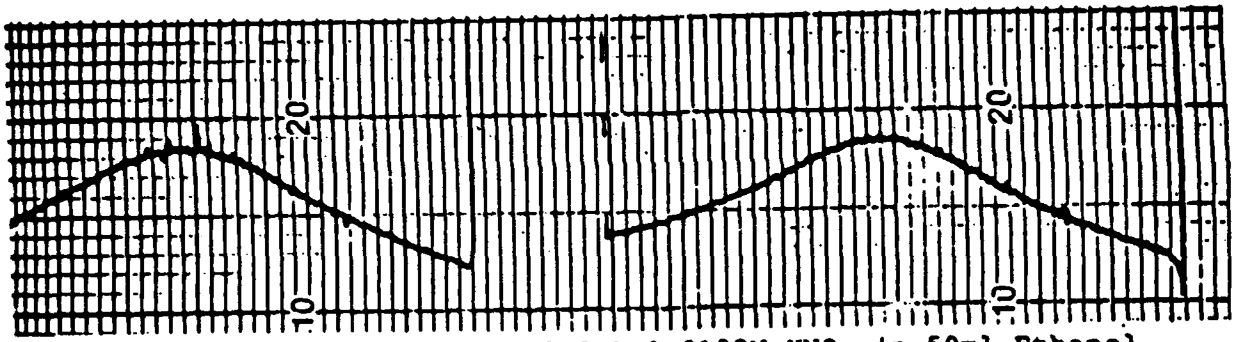
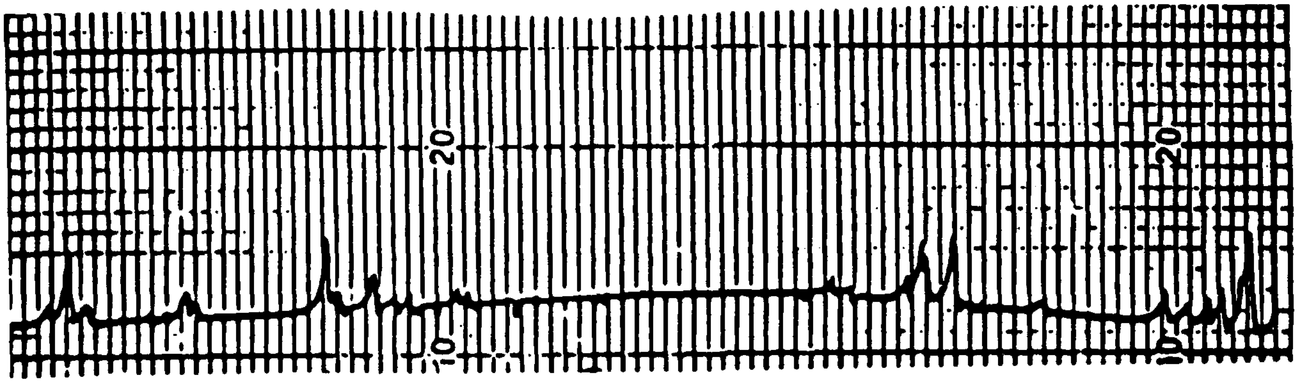


Figure 1. Nitric acid titration, % recovery versus sample weight



0.5gms LP 1846-03-08 + 255µl 0.0103N HNO_3 in 50ml Ethanol
Titrant 0.0095N TBAH

Figure 2. Nonaqueous titration derivative curves with optimized sample size



2.0082gms LP 1846-03-08 + 1.0ml 0.0103N HNO_3 in 50ml Ethanol

Figure 3. Nonaqueous titration derivative curve with concentrated sample

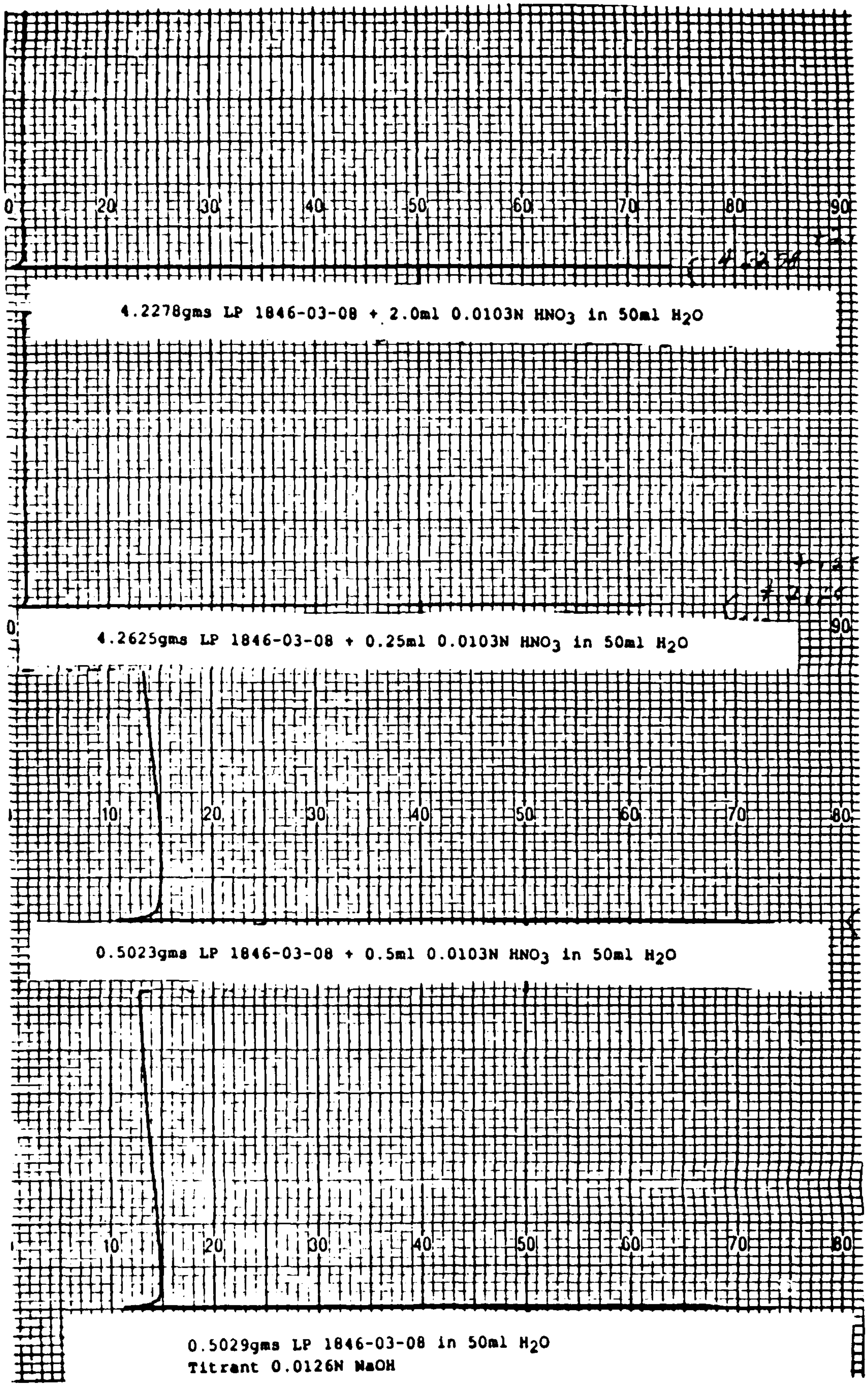
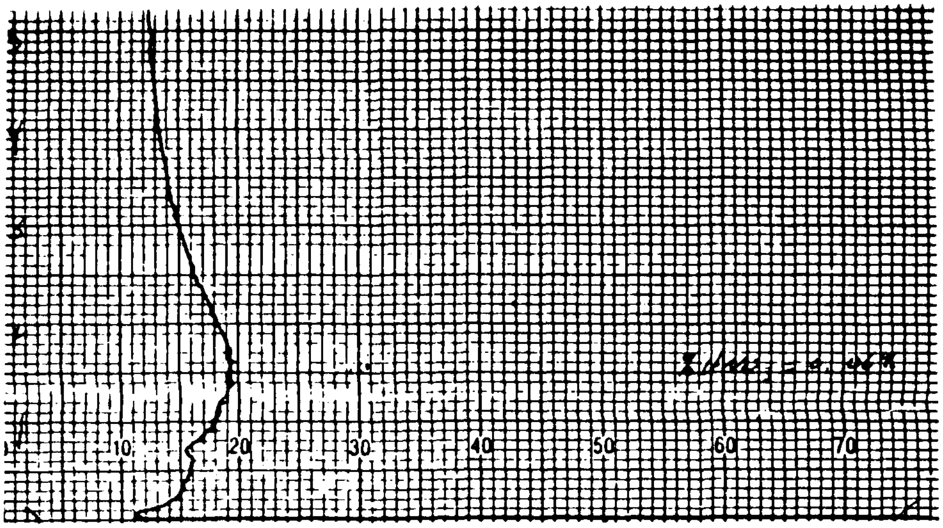
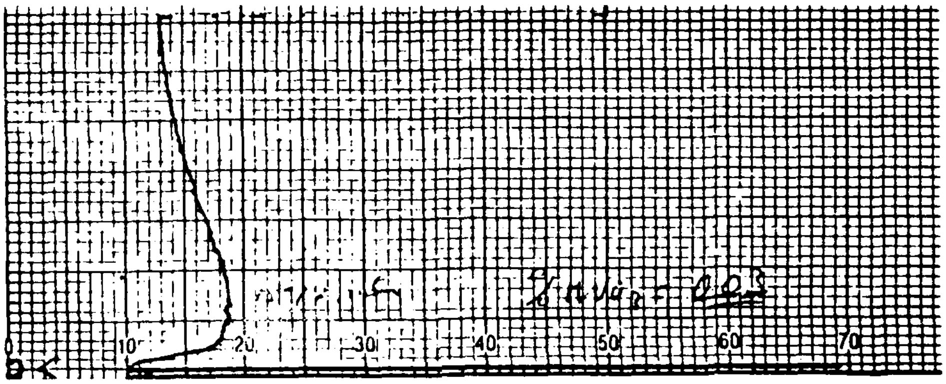


Figure 4. Effect of sample concentration in aqueous titration derivative curves



28.5340gms LP 1846-03-11 + 15ml 0.0103N HNO_3 + 25ml H_2O



28.6135gms LP 1846-03-11 + 40ml H_2O
Titrant 0.178N NaOH

Figure 5. Aqueous titration derivative curves

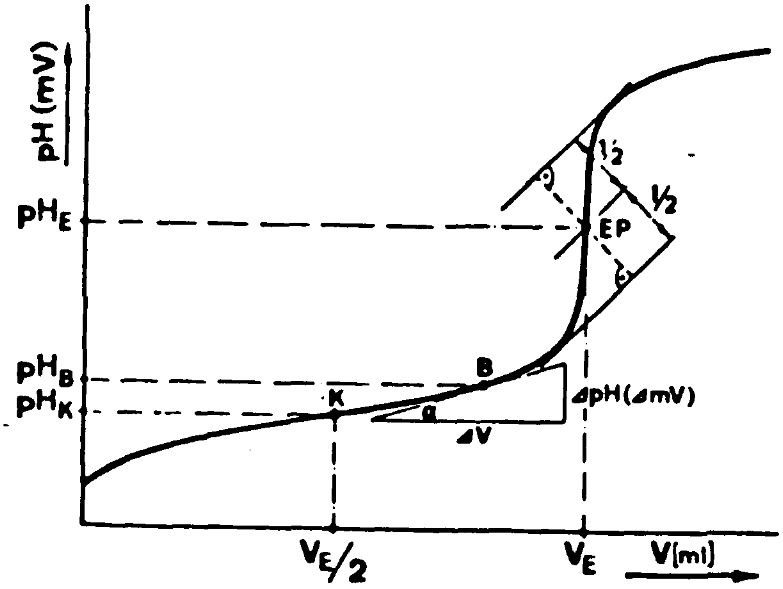
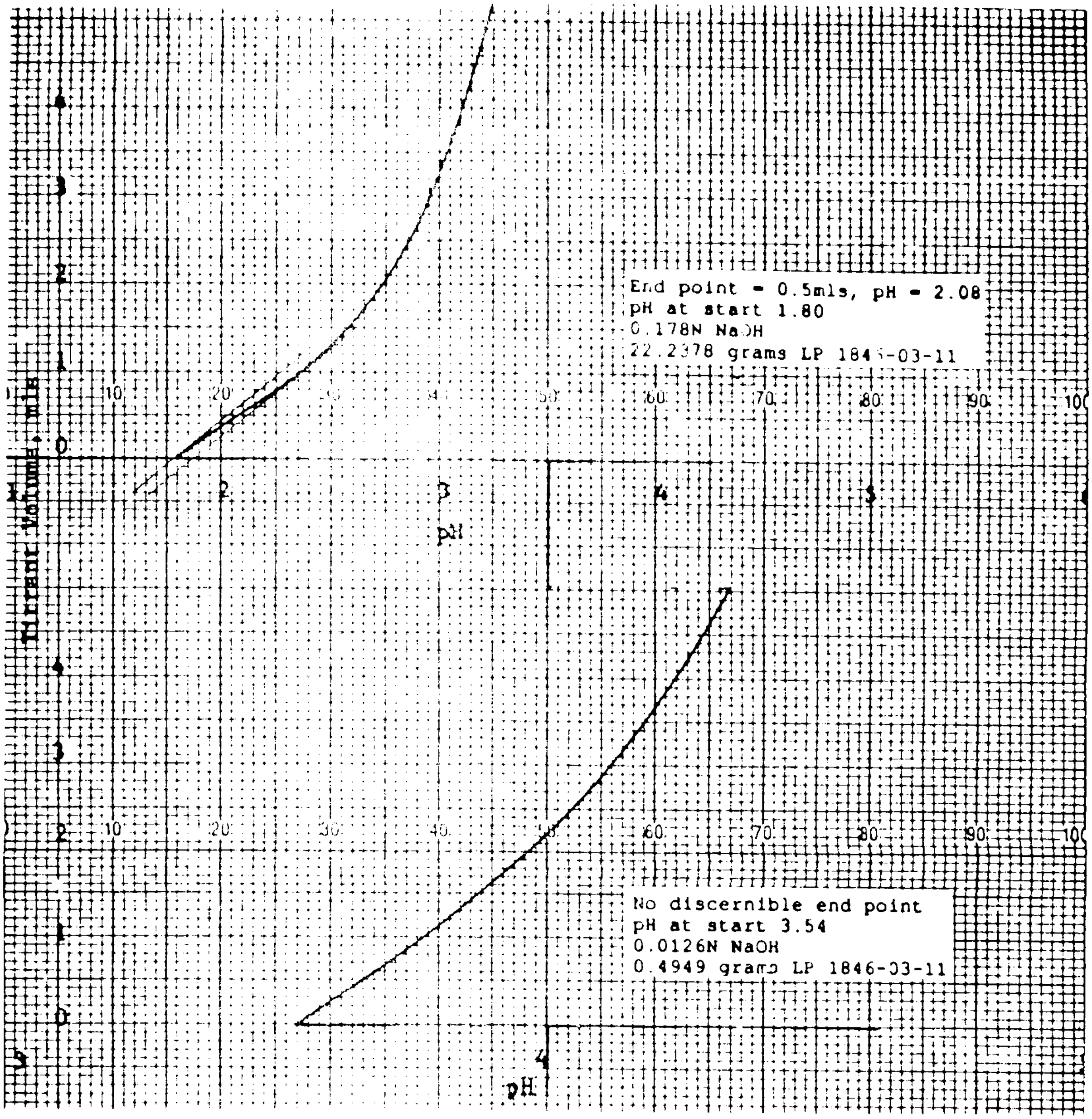


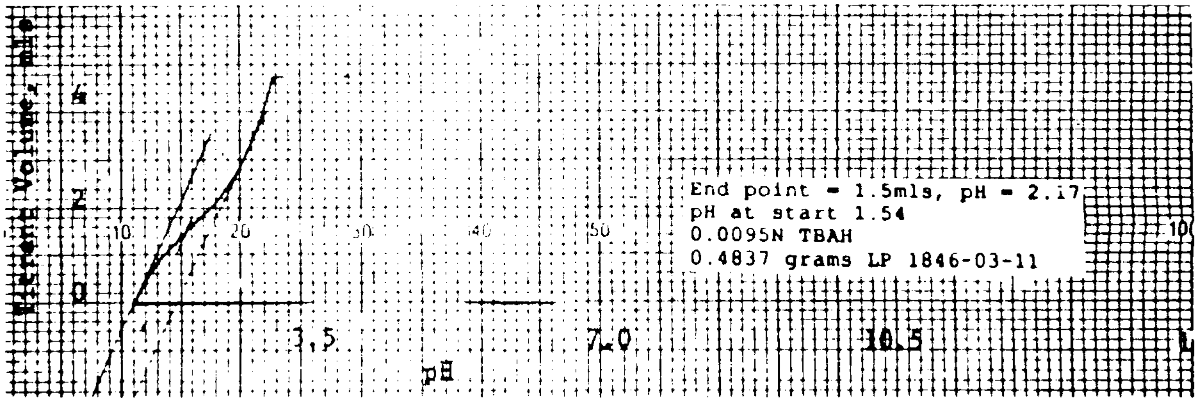
Figure 6. Potentiometric titrations S-curve



End point - 0.5mls, pH - 2.08
pH at start 1.80
0.178N NaOH
22.2378 grams LP 1846-03-11

No discernible end point
pH at start 3.54
0.0126N NaOH
0.4949 grams LP 1846-03-11

Figure 7. Aqueous titration S-curves for nitric acid



End point - 1.5mls, pH - 2.17
pH at start 1.54
0.0095N TBAH
0.4837 grams LP 1846-03-11

Figure 8. Nonaqueous titration S-curves for nitric acid

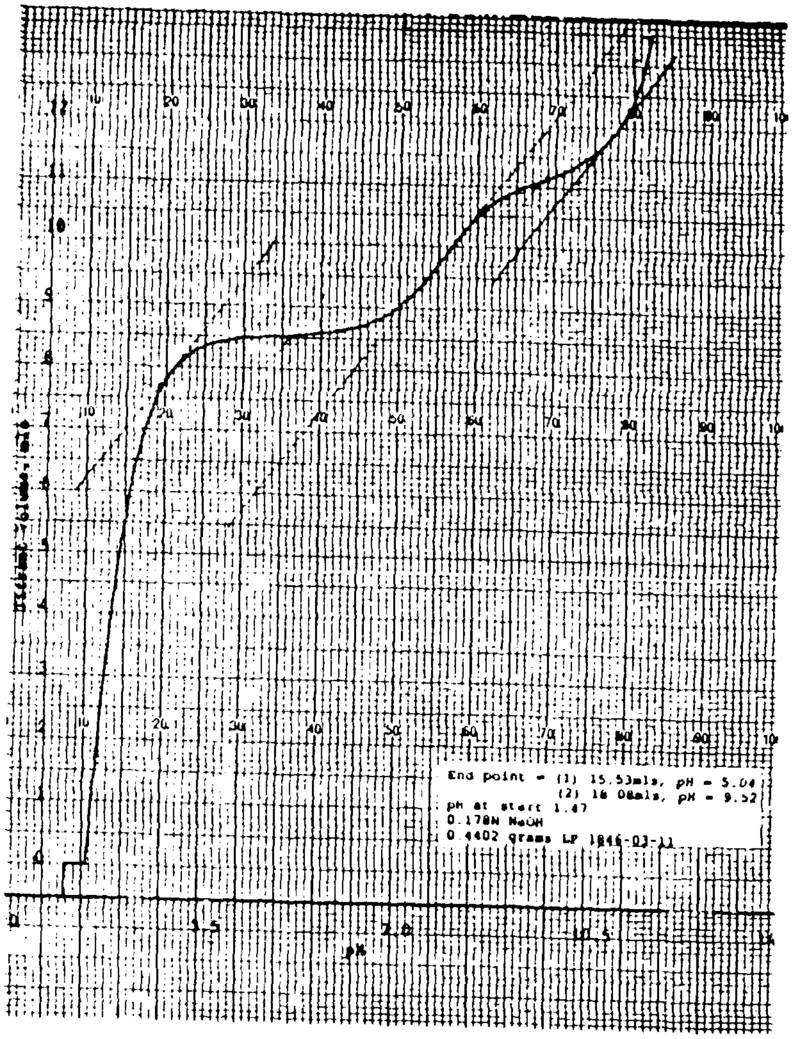


Figure 9. Aqueous titration S-curves for HAN/TEAN

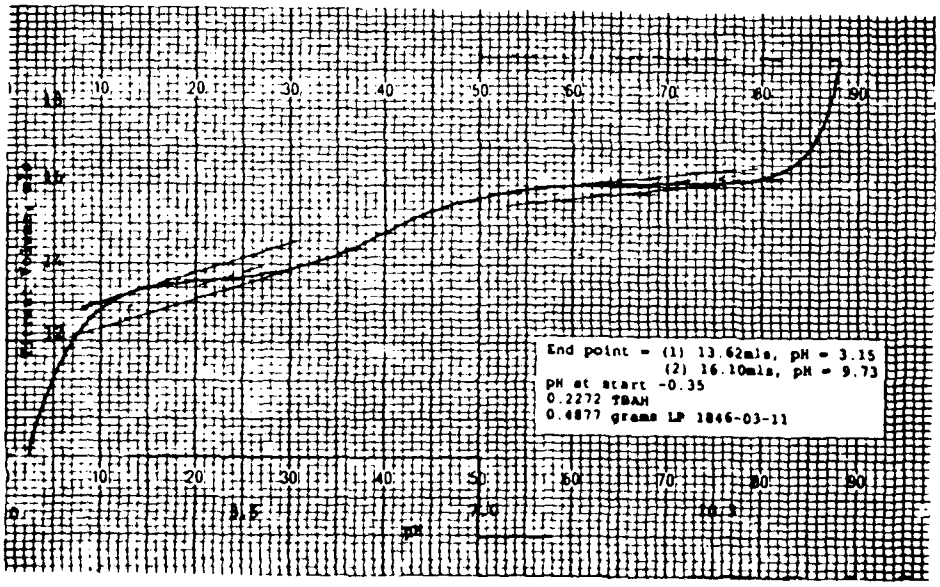


Figure 10. Nonaqueous titration S-curve HAN/TEAN

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Corrections should be made to the following reports:

1. ADA 226186 - author's name should be S. P. Griff not J. P. Griff

2. ADB 147023 - report number should be ARFSD-SP-90002 not ARFSD-SP-90004

Florence Winkelman

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