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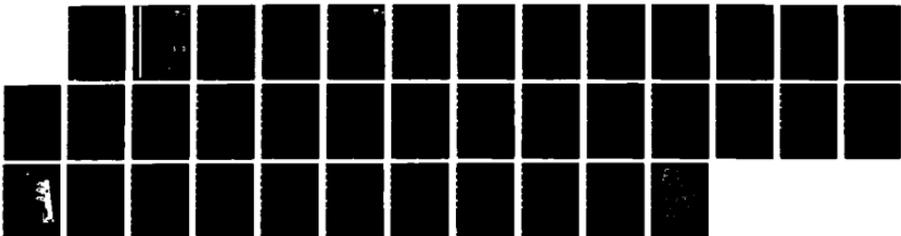
PROCESS FOR ASSESSING THE STABILITY OF HAN
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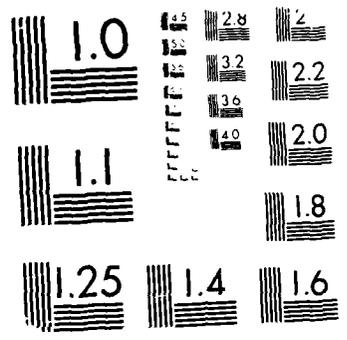
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PROCESS FOR ASSESSING THE STABILITY
OF HAN-BASED LIQUID PROPELLANTS
2nd Interim Report

by

Dr. R. Hansen
Dr. E. Backof
Dr. H. J. de Geiff

June 9, 1987

United States Army



EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY

London England

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Relative error was 0.1 - 0.2 % for HAN and 1 - 1.5 % for IPAN and TEAN. Nitric acid and AN were only present in small quantities (approx. 1 %). The relative error may here reach 25 %.

Titration in organic solvents were to be carried out and assessed later.

(Keywords:)



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1. Abstract

The Second Interim Report deals with the quantitative chemical analysis of monergol liquid propellants based on HAN. This included the components HAN (hydroxylamine), IPAN (isopropylammonium nitrate), TEAN (triethanolammonium nitrate), AN (ammonium nitrate) and free nitric acids.

As method, volumetric analysis (titration) with potentiometric (electrochemical) indication was selected. For our measurements we used the "Titroprozessor 636" (a microprocessor system) from Messrs. Metrohm AG (CH 9100 Herisau, Switzerland). We used water as solvent for the samples (i.e. no organic solvents).

The propellant components were to be determined through immediate (simultaneous) titration in a sample. HAN and AN had to be converted to derivatives (acetoxim and hexamethylene tetramine) as the case arose.

Relative error was 0.1 - 0.2 % for HAN and 1 - 1.5 % for IPAN and TEAN. Nitric acid and AN were only present in small quantities (approx. 1 %). The relative error may here reach 25 %.

Titration in organic solvents were to be carried out and assessed later.

2. Quantitative propellant analyses

2.1 Propellant components

Examples for the composition of liquid propellants are given in in Fig. 1. All propellants contain hydroxylammonium nitrate. The nitrate of an organic amine is the second propellant component. The first amine selected was isopropylammonium nitrate (IPAN). It was then found

that IPAN has bad burning kinetics /1/. At the present, its place has been taken by triethanolammonium nitrate (TEAN). HAN and amine nitrate are liquified by adding water. In view of its relatively low water content of approx. 20 % by wt., the liquid propellant mixture should rather be called a melt than a solution.

Ammonium nitrate (AN) is not listed in Fig. 1. It either occurs as an impurity in the components or is produced as a decomposition product. Even slight quantities of AN are supposed to be unfavorable for interior ballistics /1/.

2.2 Methods of determination

Separation and quantitative determination of the propellant components by gas chromatography appears to be possible. For this purpose, the amines should be liberated in preparatory column filled with alkalines. However, it is questionable whether the hydroxylamine would survive the separation process without decomposition. No examples are given in literature, and we did not carry out our own experiments.

Ion chromatography is without doubt a conserving separation process, which has been worked out for analyses in the ppm range. The necessary sample volume is approx. 100 microliters (= 0.1 ml). The individual ions are detected quantitatively by conductivity measurements. Here the accuracy of analytical determinations, however, is not reached.

For the determinations in this study we chose the method

volumetric analysis. These are accurate (generally better than 1 %). There are often several determination processes for one component (e.g. analysis via neutralization, oxidation and precipitation), which considerably improves reliability. Reference solutions, which are difficult to prepare or also have to be controlled by volumetric analysis, are not necessary. For the propellants, a number of compounds (generally three) have to be titrated one after the other. This is why simple apparatus and indication processes (chemical indication) are not sufficient. Potentiometric determination of the equivalence point is the most suitable method /2/.

Time is saved by using automatically recording titration equipment. Evaluation of titration curves by calculation is difficult where terminal titration points are weak. Therefore, the use of microprocessor-assisted titration and potentiometric equipment is not only recommendable but necessary /3/.

2.3 Acid/base titration and pK values

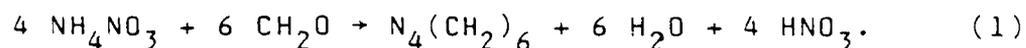
All propellant components given in Fig. 1 and in Section 2.1 are salts formed from a relatively strong acid (in this case nitric) and relatively weak bases (in this case organic and inorganic nitrogen compounds).

In aqueous solution, these salts yield an acid reaction: the pH value is below 7. The salts can therefore be titrated with a strong base, e.g. potassium hydroxide solution. The bases are then liberated from the salts (substitution titration). In the relatively stronger bases such as ammoniac and primary organic amines, the equivalence point is far into the alkaline range (above pH = 10) . The titration point can then no longer be

determined with color indicators such as e.g. phenolphthalein.

The acidity of ammonium- and hydroxylammonium salts can be increased through derivate formation. The titration points are then shifted towards lower pH values. In this way, simultaneous determinations are facilitated or made possible.

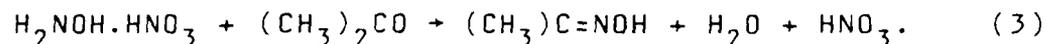
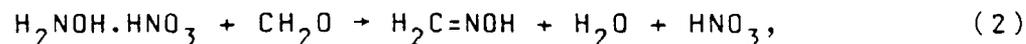
Ammonium salts react with formaldehyde to form the very weak base hexamethylene tetramine:



The sample can be titrated after the addition of formaldehyde with potassium hydroxide and phenolphthalein as indicators /4/.

The reaction is specific for ammonium salts and ammoniac. Organic amines do not react under these conditions with formaldehyde.

Hydroxylammonium salts react with aldehydes and ketones to aldoxims or ketoxims respectively. For example, formaldoxim or acetoxim is obtained from hydroxylammonium nitrate with formaldehyde or acetone:



The individual types of ion can be determined in mixtures from different acids or bases one after the other via titration if the final potentials are sufficiently different from each other. These potentials depend on the dissociation constants K_A and K_B of the relevant acids or bases.

For reference purposes, the dissociation constant or pK

value analogous to the pH value is used. This is defined as

$$pK_A = -\log K_A \text{ or } pK_B = -\log K_B.$$

The equation:

$$pH = pK_A - \log(C_{\text{acid}}/C_{\text{salt}}) \quad (4)$$

exists between the pK value of a weak acid or base in aqueous solution and the measurable pH value of the solution.

C_{acid} and C_{salt} are total concentrations of an acid and its salt known from initial weight or analysis.

Activity coefficients are negligible due to the low concentrations involved.

Where the concentrations of acid and salt are equal, the log in Eq. (4) assumes the value zero. In such a case $pH = pK_A$ or $pH = pK_B$. pK values can then be measured via potentiometric titration: the pK value is equal to the pH value measured at half neutralization.

The following relation exists between pK_A and pK_B values:

$$pK_W = pK_A + pK_B. \quad (5)$$

pK_W is the negative log of the ion product of water:

$$K_W = 0.68 \cdot 10^{-14} \text{ mol}^2 \cdot \text{dm}^{-6}; \quad pK_W = 14.17; \text{ values apply for } 20 \text{ }^\circ\text{C} (68 \text{ }^\circ\text{F}).$$

In Table 1, the values for K_A , pK_A and pK_B (columns 2, 3 and 4) have been put together for the most important propellant components.

The values are determined through neutralization titration using the "Titroprozessor 636", whereby the nitrates of the amines (column 1) were titrated with potassium hydroxide. First the pK_A values (column 3) are obtained as the pH values measured once half the final point volume of titration liquid had been used up /7/.

The single-rod glass electrode used for measuring was calibrated through comparison with two buffer solutions of a known pH value /7/.

For the pK_A determinations, as far as possible, the same test conditions were adhered to as in later measurement analyses (quantity, volume and temperature of the sample; normality of the titration liquid).

The pK_B and K_A values are calculated from the pK_A values. For reference, the pK_B values obtained from literature were entered in Table 1 (column 5). Further details on the measuring procedures used to obtain these values (potentiometry, conductivity measurements) are not known. In the case of hexamethylene tetramine (3rd row), the two literature values differ quite considerably. Under these conditions, the agreement between columns 4 and 5 is to be regarded as satisfactory.

The acidity of the amine nitrates can be seen from Table 1: the propellant components are arranged according to decreasing acidity, i.e. with a decrease in the dissociation constant K_A .

Simultaneous determinations of a number of acids or bases are only possible if the dissociation constants are greatly different. This difference should be by 4 /4/ or at least 3 /1/ times the power of ten. The situation is even less favorable where a type of ion is only

present in low quantities in a mixture such as e.g. NH_4^+ as an impurity in HAN. The equivalence point is then covered by interference of the titration curves. Nevertheless, with microprocessor-assisted titration apparatus it is still possible to identify weak and closely adjacent final titration points /3/.

2.4 The Titroprozessor 636

The Titroprozessor 636, Program Group P 100, is an analog/digital measurement and titration unit for universal potentiometric application.

The unit is equipped with a 16-bit microprocessor enabling special performance in processing and evaluating signals, data output and the control of peripheral equipment.

Titration can be carried out in three different operation modes:

- dynamic titration with variable volume steps: few measurement points with stretched and many measurement points with greatly curved sections;
- dynamic titration with variable volume steps up to the preselected final point; the addition of reagent is interrupted when a preselected final point or potential is reached;
- monotone titration at constant volume steps: measurement point accumulation with low curvature.

The evaluation programs to calculate the point of equivalence from the titration curves are based on methods known from literature /2/. Where necessary the

manufacturer (Metrohm) have applied modified evaluation methods /7/.

The manufacturer indicates that the titroprocessor 636 is capable of detecting equivalence points which cannot be recognized visually as points of inflection in the titration curve path. Differences between points of inflection and equivalence points otherwise producing erroneous results are corrected for the most part in the system.

Examples communicated by the manufacturer show that simultaneous determination is still possible where equivalence points differ by 2.5 to 3 pH units. This corresponds to just as many pK units or the factor 300 to 1,000 in the K_A values. The performance limits of the Titroprozessor 636 for simultaneous determination appear to have been reached here.

Fig. 2 shows the Titroprozessor 636 with its propellants analysis setup. For titration, the apparatus incorporates 2 motor piston burettes of the Dosimat 635 type and a motor piston burette of the type Dosimat 665 (with integrated microprocessor) as well as a magnetic stirrer with sample container and holder for indicator electrode. The three motor piston burettes allow freely selectable addition of measurement solutions (for example 0.5 N or 0.05 N KOH, 1 N NH_4NO_3 solution) and the dosage of auxiliary substances (for example acetone or formaldehyde solution).

A combined pH glass electrode ("single-rod measurement chain") with a U glass membrane is used as an indicator.

The control card for the Titroprozessor 636 is shown on the right in Fig. 2. The cards are used for operation and calculation modes and programmed by "rubbing on"

square black code markings.

2.5 Propellant analyses

2.5.1 NOS-365

As shown in Fig. 1, the propellant NOS-365 contains approx. 61 %/ wt. hydroxylammonium nitrate (HAN), 19 %/wt. isopropylammonium nitrate (IPAN) and 20 %/wt. water. It can be seen from Section 2.4 and Table 1 that the simultaneous titration of HAN and IPAN is possible with strong base without difficulty. This is confirmed by the titration curve printed out by the titroprocessor in Fig. 3. The final titration point (1) of the first component determined (HAN) is clearly prominent as a point of inflection, as the K_A values of HAN and IPAN differ by the factor $5.3 \cdot 10^4$. The final point of the IPAN determination (2) is, however, difficult to recognize without additional help, which is due to the high alkaline value of the primary amine. Fig. 3.1, which shows the 1st derivative of the titration curve from Fig. 3, makes this clear. In the 1st derivative, the turning points appear as extreme values (max. or min.). The point of equivalence (2) is now only recognizable as the crossing point of two almost straight curve sections. Therefore, the accuracy obtainable through titration with HAN should doubtlessly not be expected from the IPAN determination.

The influence of derivate formation can be seen from Fig. 4:

With hydroxylamine, acetone forms acetoxim, and the final point (1) in the determination of HAN is shifted into the acid range. The change in pH in the equivalence range is in fact so great that a chemical

determination of the final point with color indicator, e.g. Methyl Red, could be possible. The quotient from the corresponding K_A values amounts to $1.4 \cdot 10^3$. This is the highest value which can be calculated from Table 1 at all. As can be seen from Fig. 4.1, Equivalence Point (2), the formation of derivate changes nothing for the determination of IPAN.

Figs. 5 and 5.1 document the simultaneous titration of 3 substances, i.e. HAN, IPAN and AN (ammonium nitrate). The final titration points must be drawn apart from each other through a two-time derivate formation (formation of acetoxim and hexamethylene tetramine through successive additions of acetone or formaldehyde solution accordingly). The quotients of the K_A values are $1.4 \cdot 10^4$ for the separation of HAN and AN and $1.0 \cdot 10^5$ for the separation of AN and IPAN (Table 1). The quotients are sufficiently large for the separations. As the quantity of AN is only low in the sample (generally below 0.5 %/wt.), it must be enlarged by adding a known quantity of ammonium nitrate to make separation possible.

With this method, the real AN content of the propellant is calculated as a difference in figures having practically the same magnitude. In such cases the accuracy attainable is only moderate. On the other hand, the determination of substances only present in small concentrations (example: less than 1 %/wt.) with less accuracy is sufficient.

2.5.2 LP 1845 and LP 1846

The LP 1845, which can be considered as a successor of NOS-365 (comp. Section 2.1) contains, as correspondingly

given in Fig. 1, 63 %/wt. HAN, 20 %/wt. TEAN and 17 %/wt. water.

In connection with stability tests on LP 1845, the question arose as to whether the propellant contains free acids or free bases. Simple pH measurement is less informative as the propellant mixture acts as a buffer. We therefore tried to recognize and determine the free acid (nitric acid) possibly present in the propellant by potentiometric titration. Fig. 6 shows the titration tests with 0.05 N potassium hydroxide solution. The point of inflection of the titration curve is identified by the microprocessor as the equivalence point (1) with a flat but clear maximum in the 1st derivative. The content of free nitric acid was determined at 0.31 %/wt.; a value which appears to be rational.

Titration curves obtained during a simulation titration of HAN and TEAN are reproduced in Figs. 7 and 7.1. The separation of HAN and TEAN by simple substitution titration is not possible as the quotient of the K_A values is only $6.5 \cdot 10^1$. After the formation of acetoxim, the K_A quotient reaches the value $10.6 \cdot 10^6$, and separation is possible without further difficulty. The final point of TEAN titration is also well indicated as triethanolamine - contrary to isopropylamine - belongs to the weak amine bases. The titration curve according to Fig. 7 therefore represents the typical example of a simultaneous titration process. This is especially confirmed by the sharp max. values in Fig. 7.1.

Opposed to this, the simultaneous titration of TEAN and AN is not possible. In the separation of AN (after the formation of hexamethylene tetramine nitrate) and TEAN, the K_A quotient only reaches the value of $1.3 \cdot 10^2$

and, without the formation of derivatives, only as much as $3.4 \cdot 10^1$.

The increase in the quantity of ammonium nitrate in the sample caused the inflection points to appear in the titration curve. The inflection points did not agree with the equivalence points. The differences once more depend on the quantity of ammonium nitrate in the sample. Corrections are complicated and uncertain. They are therefore not taken into consideration.

It was found that AN can be determined through the known process of ammoniac distillation from a sample made alkaline. The method works because triethanolamine is not volatile with water steam. Hydroxylamine can be oxidized quantitatively to dinitrogen oxide (N_2O) in a sample with Fehling's solution (Cu^{2+} -tartrate complex in alkaline solution). No ammoniac as by-product is produced in the process of oxidation here. With the distillation method, it is still possible to determine 0.1 %/wt. AN reliably.

The water content of liquid propellants on the basis of HAN according to Fig. 1 can be determined directly by Fischer titration. This method requires a special unit, as the Titroprozessor 636 is not suited for this. The presence of amines and particularly the reductively acting hydroxylamine may lead to disturbances. Such disturbances can be avoided if the Work Specifications recommended by Messrs. Riedel-de Haen are followed /8/.

2.6 Accuracy of the analytic determinations

If, in the chemical analysis of the quantity X (e.g. the content of HAN in %/wt.), n individual tests are

carried out, the most probable value is the arithmetical mean \bar{X} (X transverse):

$$\bar{X} = \sum X/n \quad (6)$$

As measure for the scattering of the individual values, the standard deviation s (also sigma - 1) is most frequently used /9, 10/:

$$s = \sqrt{\frac{(X - \bar{X})^2}{n - 1}} = \sqrt{\frac{\sum X^2 - (\sum X)^2/n}{n - 1}} \quad (7)$$

\bar{X} and s are given in the same unit, e.g. in mol/kg or frequently in percentage by weight (%/wt.) in chemical analysis methods. The measurements are especially accurate or inaccurate where s is small and \bar{X} large or vice versa. To determine the accuracy of analysis, therefore, both values must be communicated. This means that the variation coefficient V is an instructive parameter for measurement error:

$$V = s \cdot 100/\bar{X} \quad (8)$$

The variation coefficient is given in relative percent (%).

In Table 2, the statistical quantities \bar{X} , s , V and n have been drawn up for analysis of the three propellants NOS-365, LP 1845 and LP 1846. The compounds HAN, IPAN, TEAN, AN and HNO_3 were determined. Unfortunately it was not always feasible due to the amount of work involved to follow through a sufficiently large number n (column 5) for individual determinations. It can nevertheless be recognized that the major component HAN can be determined the most accurately. The variation coefficient V (column 4) is between 0.15 and 0.2 %, this being a good result for a simultaneous determination.

The determination of IPAN and also TEAN had less accurate results. In the case of these components, V had the value 1 - 1.5 %. The reasons for this have already been mentioned in Section 2.5.1: there is an unfavorable formation of the titration curve (figs. 3 and 3.1) and, in comparison to HAN, a lower quantity in the mixture. In the case of ammonium nitrate, the V values are at their worst: 13 - 27 %. This is principally due to the fact that determination of AN is the most difficult individual measurement in the analysis of propellants. However, the comparatively high relative errors are tolerable at the low AN contents involved. Free nitric acid is also only present in small quantities in propellants, but the determination is easier than in the case of ammonium nitrate. The variation coefficient is correspondingly between 3 and 11 %.

3. Conclusions

We have been able to show that the simultaneous titration of HAN-based liquid propellants with water as a solvent is possible if modern processes (potentiometry) and modern apparatus is used.

The attainable accuracy is good for HAN and sufficient for the other components.

An improvement of accuracy appears to be possible as experience with the methods used increases.

We have planned to test titration processes with organic solvents. Testing aims at finding out whether expensive and complicated work methods can be justified by the advantages to be expected (better separation of the components, greater measurement accuracy).

4. Literature

- /1/ Klein, N.
USA Ballistic Research Laboratory
Private communication
- /2/ Kraft, G.; Fischer, J.
Indikation von Titrationen (The Indication of
Titrations)
W. de Gruyter Vlg, Berlin 1972
- /3/ Henze, H., Neeb, R.
Elektrochemische Analytik (Electrochemical
Analysis), page 65, Springer-Verlag,
Berlin/Heidelberg 1986
- /4/ Poethke, W.
Praktikum der Maßanalyse (Practical Guideline on
Measurement Analysis),
Verlag Harri Deutsch, Thun und Frankfurt 1980
- /5/ Huber, W.
Titrationen in nichtwässrigen Lösungsmitteln
(Titrations in non-aqueous solvents),
Akademische Verlagsgesellschaft, Frankfurt am
Main 1964
- /6/ Ullmanns Encyklopädie der technischen Chemie
(Encyclopedia of Technical Chemistry),
4. Auflage/edition, Bd./vol. 7, page 386
Verlag Chemie, Weinheim/Bergstr. 1974
- /7/ Firmenschrift der Metrohm AG in CH-9100 Herisau:
Gebrauchsanweisung für den Titroprozessor 636
(Operator's Manual for the Titroprozessor 636),
Programmgruppe P 100

- /8/ Firmenschrift der Riedel-de Haen AG in 3016
Seelze 1: Hydranal, Wasserreagenzien nach Eugen
Scholz für die Karl-Fischer-Titration (Guidelines
by Messrs. Riedel-de Haen for Titration according
to the Karl Fischer Method), 3. Auflage/Ed. 1982
- /9/ G. Jander and K. F. Jahr:
"Maßanalyse, Theorie und Praxis der Titrationsen
mit chemischen und physikalischen Indikationen"
(Volumetric analysis, theory and practice of
titrations with chemical and physical
indications), neubearbeitet (new edition) von G.
Schulze und J. Simon, W. de Gruyter Vlg., Berlin,
New York, 1986, 14. Auflage/Edition
- /10/ R. Kaiser and G. Gottschalk:
"Elementare Tests zur Beurteilung von Meßdaten"
(Elementary tests on the assessment of
measurement data), B. I. Hochschultaschenbücher
Band 774, bibliographisches Institut Mannheim/
Wien (Vienna)/Zürich 1972

5. Annex (tables and figures)

Tab. 1: Dissociation constants K_A as well as relevant pK_A and pK_B values of several propellant components in aqueous solution at 20 °C.

Tab. 2: Characteristics X , s , V and n for the statistical evaluation of propellant analyses

Fig. 1: Composition of liquid propellants

Fig. 2: The Titroprozessor 636 with propellant analysis section

Fig. 3: Analysis of NOS-365
Simultaneous determination of HAN and IPAN by substitution titration: titration curve

Fig. 3.1: Analysis of NOS-365
Simultaneous determination of HAN and IPAN by substitution titration: 1st derivative of titration curve

Fig. 4: Analysis of NOS-365
Simultaneous determination of HAN and IPAN by substitution titration after formation of acetoxim by acetone additive: titration curve

Fig. 4.1: Analysis of NOS-365
Simultaneous determination of HAN and IPAN by substitution titration after formation of acetoxim by acetone additive: 1st derivative

Fig. 5: Analysis of NOS-365
Simultaneous determination of HAN, IPAN and AN by substitution titration:
Here: determination of HAN after formation of acetoxim by the addition of acetone

Fig. 5.1: Analysis of NOS-365: Simultaneous determination of HAN, IPAN and AN by substitution titration: titration curve (top) and 1st derivative (bottom).
Here: 1) Determination of AN after the addition of ammonium nitrate at a known quantity and the addition of formaldehyde (formation of hexamethylene tetramine)
2) determination of IPAN

Fig. 6: Analysis of LP 1845: Determination of free nitric acids: titration curve (top) and 1st derivative (bottom)

Fig. 7: Analysis of LP 1845: Simultaneous determination of HAN and TEAN by substitution titration: Titration curve.
Here: 1) Determination of HAN after acetoxim formation by the addition of acetone
2) Determination of TEAN

Fig. 7.1: Analysis of LP 1845: Simultaneous determination of HAN and TEAN by substitution titration: 1st derivative.
Here: 1) Determination of HAN after acetoxim formation by the addition of acetone
2) Determination of TEAN

Table 1

Dissoiation constants K_A as well as relevant pK_A - and pK_B values in a number of propellant components in aqueous solution at 20 °C.

No.	Propellant Components	K_A mol ² dm ⁻⁶	pK_A	pK_B	pK_B (literature values)	Literature quote
		2	3	4	5	6
1	Hydroxylammonium nitrate (HAN) + formaldehyde (formaldoxim)	$0,245 \cdot 10^{-1}$	1,61	12,56	./.	./.
2	Hydroxylammonium nitrate (HAN) + acetone (acetoxim)	$0,191 \cdot 10^{-1}$	1,72	12,45	12,19	5
3	Ammonium nitrate (AN) + formaldehyde (hexamethylene tetramine)	$0,141 \cdot 10^{-5}$	5,85	8,32	8,85 9,1	6 4
4	Hydroxylammonium nitrate (HAN)	$0,733 \cdot 10^{-6}$	6,135	8,035	8,03	5
5	Triethanol ammonium nitrate (TEAN)	$0,112 \cdot 10^{-7}$	7,95	6,22	6,23	5
6	Ammonium nitrate (AN)	$0,331 \cdot 10^{-9}$	9,48	4,69	4,75	5
7	Isopropyl ammonium nitrate (IPAN)	$0,138 \cdot 10^{-10}$	10,86	3,31	3,37	5

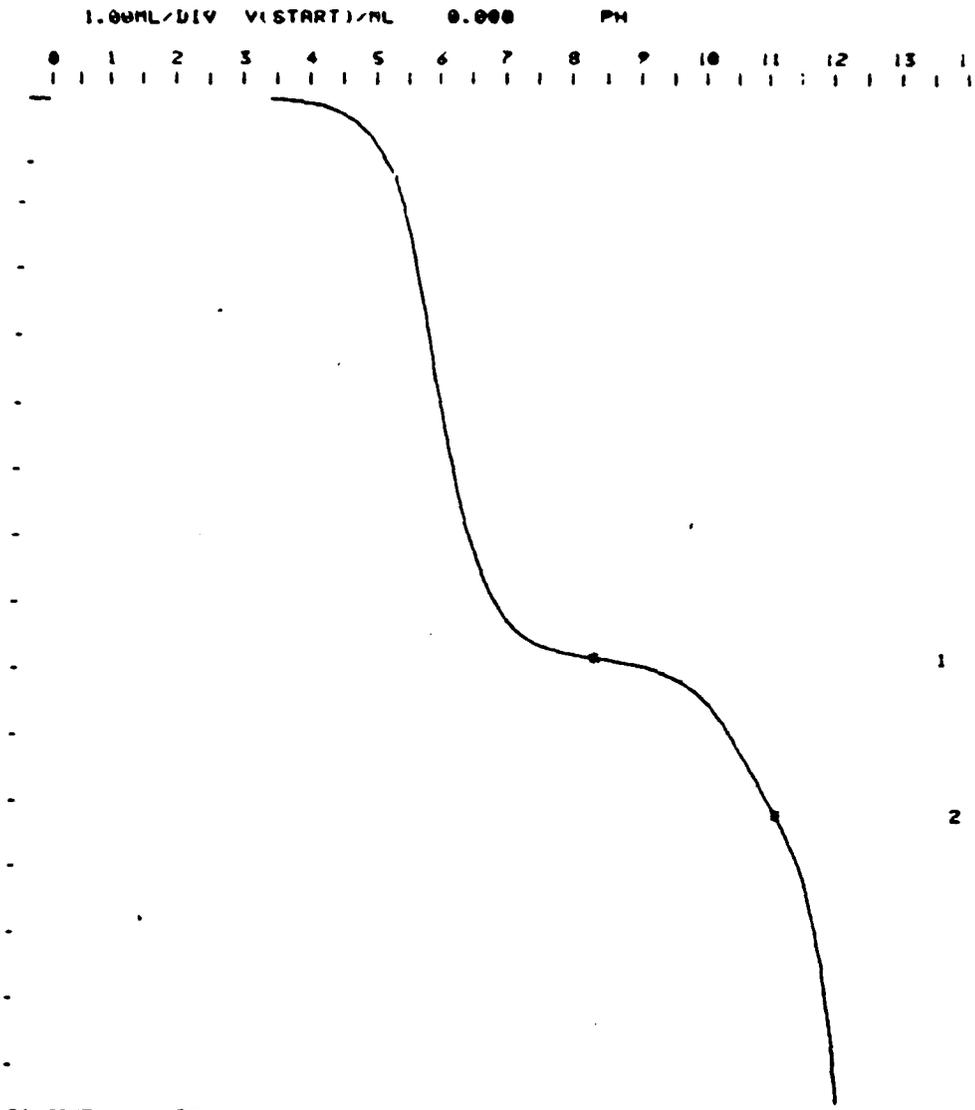
Table 2 The characteristics \bar{X} , s, V and n in the statistical evaluation of propellant analyses

Propellant	No.	Com- ponent	\bar{X} in wt. %	s in wt. %	V in rel. %	n
		1	2	3	4	5
NOS-365	1	HAN (alkalim.)	58,58	0,11	0,18	19
	2	HAN (oxidim.)	58,37	0,075	0,13	3
	3	IPAN	17,76	0,261	1,47	9
	4	AN	1,48	0,39	26,35	9
	5	HNO ₃	0,25	0,026	10,6	3
LP 1845	6	HAN	62,90	0,12	0,18	12
	7	TEAN	19,77	0,38	1,91	12
	8	AN	0,47	0,06	13,7	2 (!)
	9	HNO ₃	0,31	0,0082	2,63	4
LP 1846	10	HAN (alkalim.)	61,37	0,074	0,121	11
	11	HAN (oxidim.)	60,90	0,027	0,04	3
	12	TEAN	18,60	0,2	1,07	3
	13	AN	0,53	-	-	3
	14	HNO ₃	0	-	-	-

Code name	Combustion mat.			Oxygen balance [%]	Impulse [J/g]	Flame temperature [K]
	Symbol [wt. %]	HAN [wt. %]	Water [wt. %]			
NOS-365	IPAN 19,29	60,71	20,0	0,01	928,5	2560
LP-1776	TMAN 19,3	60,8	19,9	0,03	960,7	2600
1781	EOAN 32,5	50,3	17,2	- 0,0	929,6	2560
1812	TEN 13,6	67,5	18,9	- 0,04	959,8	2670
1814	TEN 13,2	65,3	21,5	- 0,1	924,7	2500
1835	TEN 11,8	68,4	19,8	+ 3,25	885,7	2410
1845	TEAN 20,0	63,2	16,8	- 0,05	982,3	2730
1846	TEAN 19,2	60,8	20,0	- 0,01	934,5	2570
1848	TEAN 14,5	66,3	19,2	+ 6,78	820,7	2260

IPAN ...	Isopropylammonium nitrate	$(\text{CH}_3)_2\text{CHNH}_2 \cdot \text{HNO}_3$
TMAN ...	Trimethylammonium nitrate	$(\text{CH}_3)_3\text{N} \cdot \text{HNO}_3$
EOAN ...	Ethanol ammonium nitrate	$\text{CH}_2\text{CH}_2\text{NH}_2 \cdot \text{HNO}_3$
TEN ...	Triethylammonium nitrate	$(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HNO}_3$
TEAN ...	Triethanol ammonium nitrate	$(\text{HOCH}_2\text{CH}_2)_3\text{N} \cdot \text{HNO}_3$

Fig. 1: Composition of liquid propellants



ROUTINE # 201
 # 3 PH(INIT) 3.416 V(TE)/ML 16.245
 1 V/ML 8.826 PH 8.600
 2 V/ML 11.149 PH 11.455

R1 58.8498 % HAN
 R2 19.6937 % (IPAN+NH₄NO₃)

C1 1.00000 C2 48.8200 C3 41.8480 C4 7.20200
 C5 7.20200
 DATE 22.10.84 NAME J_a

Fig. 3: Analysis of NOS-365
 Simultaneous determination of HAN and IPAN
 by substitution titration: titration
 curve

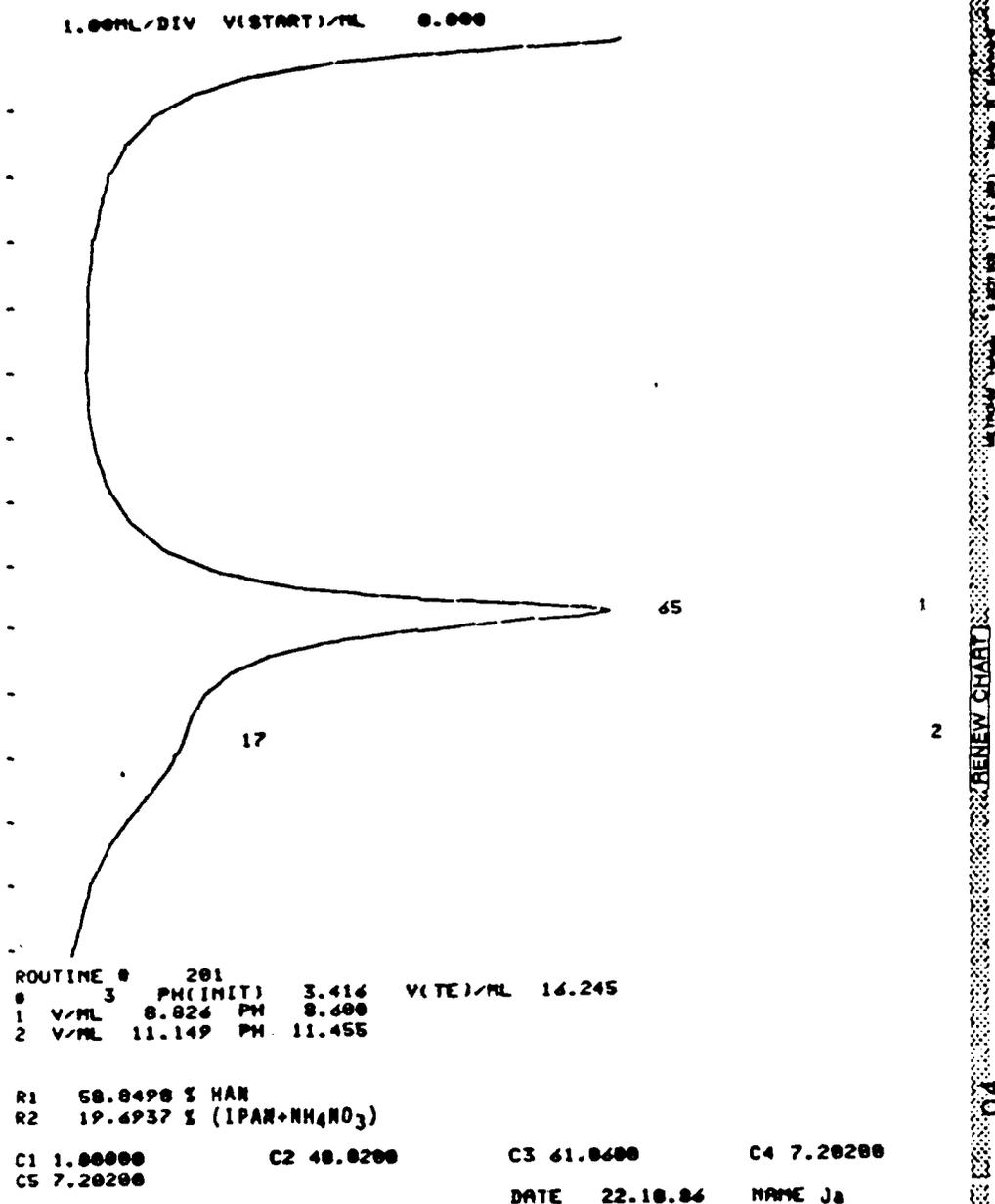


Fig. 3.1: Analysis of NOS-365
 Simultaneous determination of HAN and IPAN
 by substitution titration: 1st
 derivative of titration curve

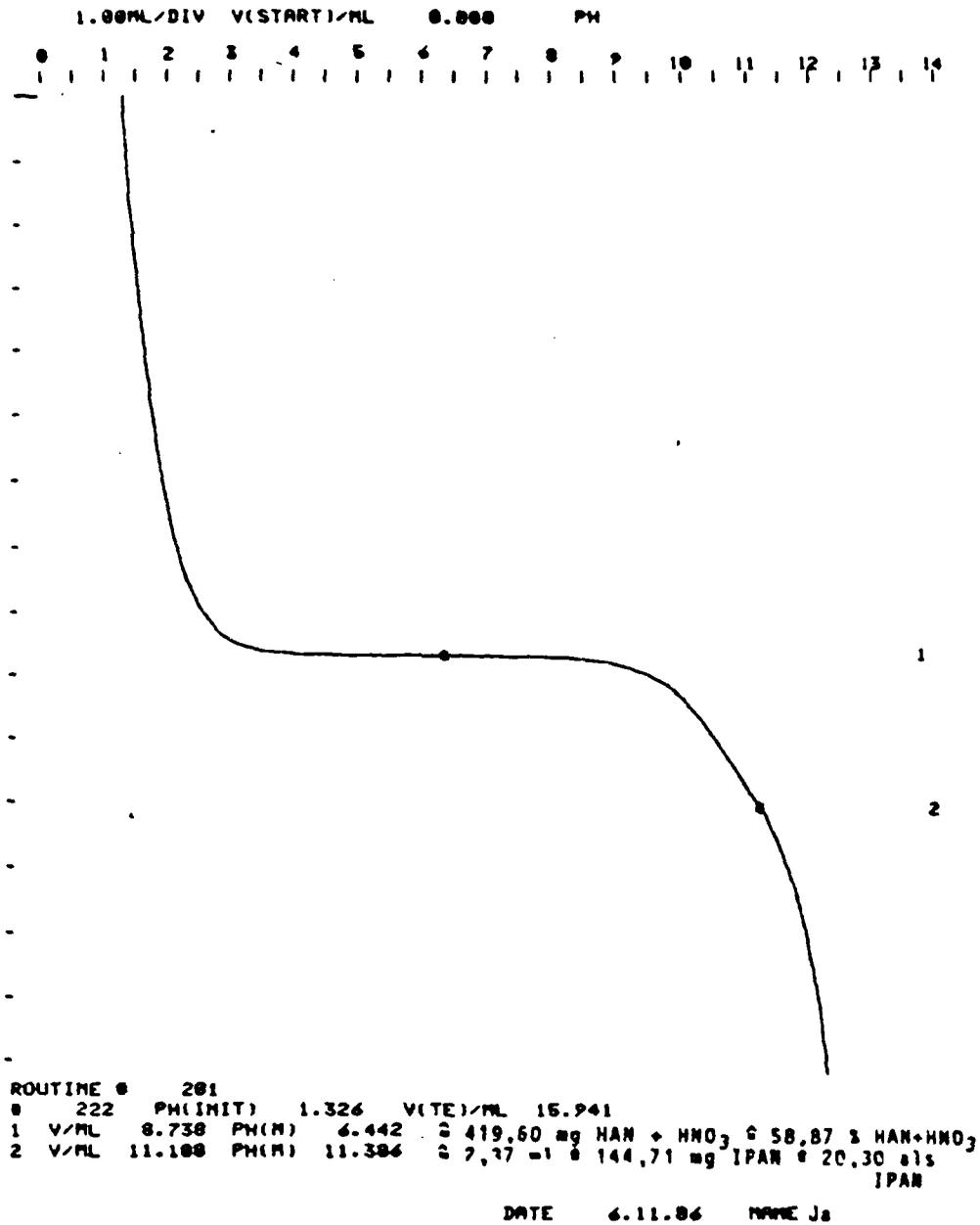
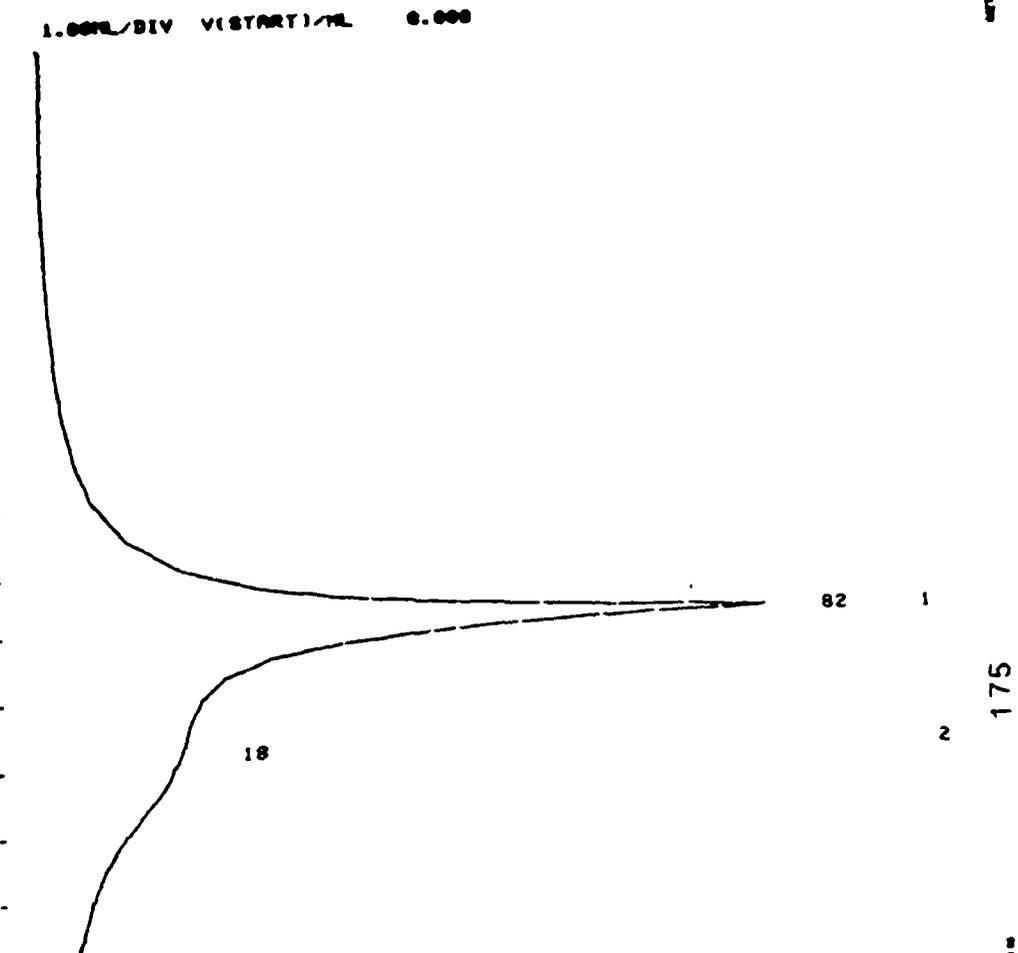


Fig. 4: Analysis of NOS-365
 Simultaneous determination of HAN and IPAN
 by substitution titration after
 formation of acetoxim by acetone additive:
 titration curve



ROUTINE 0 201
 0 222 PH(INIT) 1.326 V(TE)/ML 15.941
 1 V/ML 8.738 PH(M) 6.442 @ 419.60 mg HAN+HNO₃ @ 58.87 % HAN+HNO₃
 2 V/ML 11.100 PH(M) 11.386 @ 2.37 ml @ 144.71 mg IPAN @ 20.30 % als
 DATE 6.11.86 NAME JA IPAN

BUR.2 V/ML	20.0	ROUTINE 0	201
TEMP/C	18.0	REAGENT	0.5 n KOM wBr. Titrisol
KINET D	8.0	TITER	1.000
MPD VAR	0.0	ELECTRODES	2 kombinierte Glaselektrode Metrohm, geicht
START V/ML	0.000	SAMPLE	712,8 mg NOS 365 + 10 ml Aceton
STOP PH	100.000	REMARKS	
STOP V/ML	20.000		
STOP @ EP	7.0		
PAUSE/S	0.0		
EP-CRIT	6.0		
ADD V/ML	0.000		
EP-M LIMI	0.000		
PH LIN2	14.000		
0106			

Fig. 4.1: Analysis of NOS-365
 Simultaneous determination of HAN and IPAN
 by substitution titration after
 formation of acetoxim by acetone additive:
 1st derivative

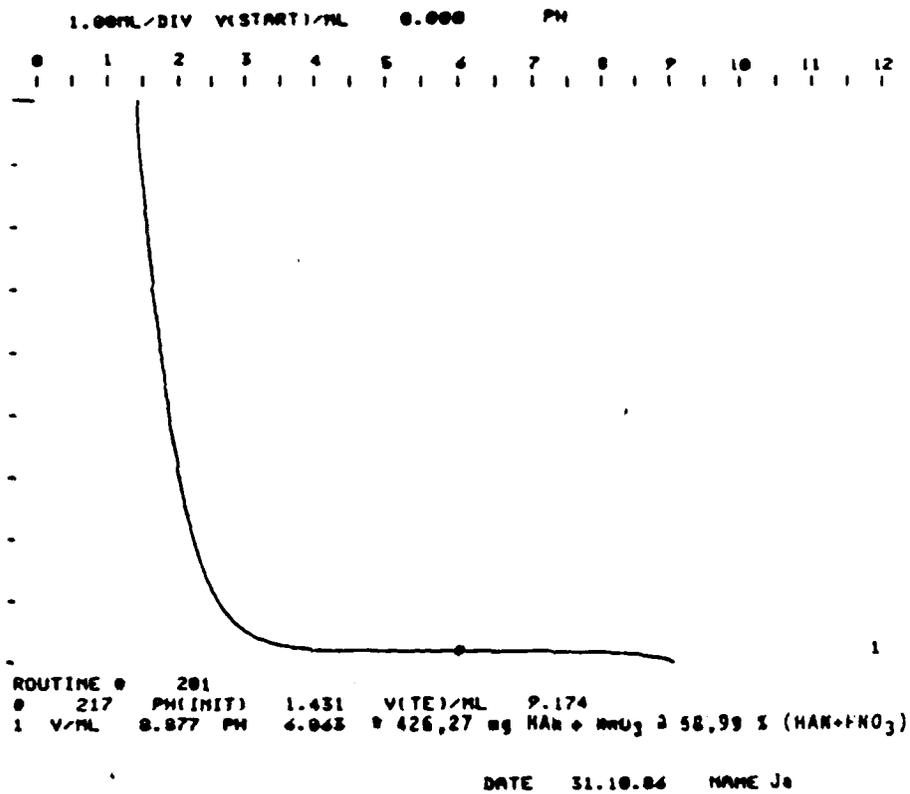
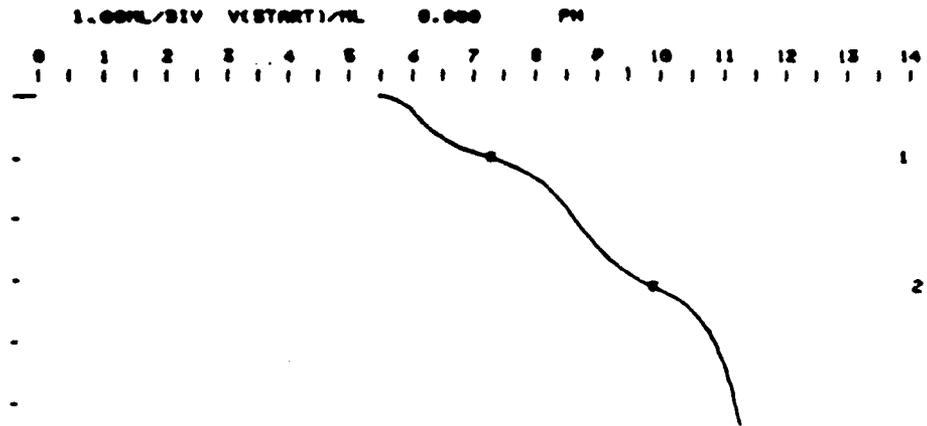


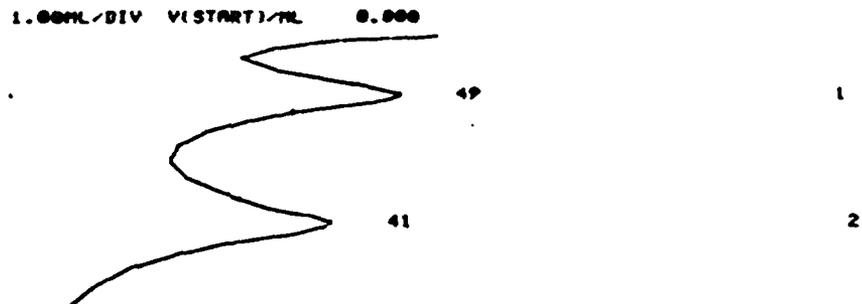
Fig. 5: Analysis of NOS-365
 Simultaneous determination of HAN, IPAN and AN by substitution titration:
 Here: determination of HAN after formation of acetoxim by the addition of acetone



ROUTINE # 1
 0 217 PH(INIT) 6.485 V(TE)/ML 5.848
 1 V/ML 1.000 PH 7.311
 2 V/ML 3.003 PH 9.940 # 2,074 ml # 126,64 mg IPAN # 17,53 % IPAN

DATE 31.10.86 NAME Ja

BUR.2 V/ML 10.0 ROUTINE # 201
 TEMP/C 25.0 REAGENT 0,5 n NaOH wBr. Titrisol
 KINET D 8.0 TITER 1,000
 HPD VAR 8.0 ELECTRODES 2 Kumbinerte Glaselektrode Metrohm
 START V/ML 0.000
 STOP PH 106.000 SAMPLE 722,6 mg NOS 365 + 10 ml Aceton (HAN-Best.)
 STOP V/ML 10.000 + 5 ml Formaldehyd 37 %
 STOP # EP 9.0 + 406,9 mg NH₄NO₃ Lsg. (=38,61 mg 100 %)
 PAUSE/S 0.0
 EP-CRIT 5.0 REMARKS
 ADD V/ML 0.000
 EP-W LIM1 0.000
 PH LIM2 14.000
 0105

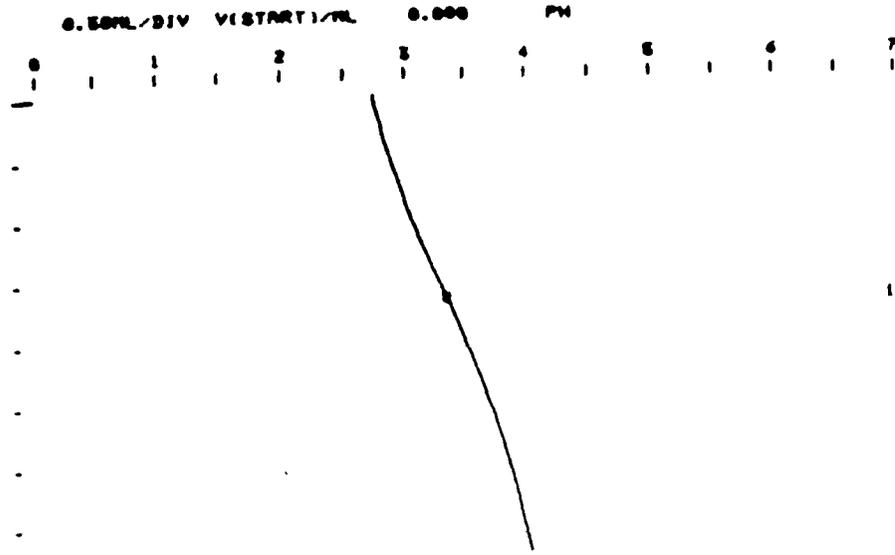


ROUTINE # 1
 0 217 PH(INIT) 6.485 V(TE)/ML 5.848
 1 V/ML 1.000 PH 7.311 # 426,27 mg (HAN+HNO₃) # 58,99 % (HAN+HNO₃)
 2 V/ML 3.003 PH 9.940 # 2,074 ml # 126,64 mg IPAN
 # 17,53 % IPAN

DATE 31.10.86 NAME Ja

Fig. 5.1: Analysis of NOS-365: Simultaneous determination of HAN, IPAN and AN by substitution titration: titration curve (top) and 1st derivative (bottom).

- Here: 1) Determination of AN after the addition of ammonium nitrate at a known quantity and the addition of formaldehyde (formation of hexamethylene tetramine)
 2) determination of IPAN



ROUTINE # 201
 # 242 PH(INIT) 2.757 V(TE)/ML 4.116
 1 V/ML 1.651 PH(M) 3.361

DATE 10.11.86 NAME



ROUTINE # 201
 # 242 PH(INIT) 2.757 V(TE)/ML 4.116
 1 V/ML 1.651 PH(M) 3.361 5,20 mg HNO₃ 0,31 % HNO₃

DATE 10.11.86 NAME Ja

BUR.2 V/ML 10.0
 TEMP/C 21.0
 KINET D 0.0
 RPS VAR 0.0
 START V/ML 0.000
 STOP PH 100.000
 STOP V/ML 10.000
 STOP # EP 7.0
 PAUSE/S 0.0
 EP-CRIT 5.0
 ADD V/ML 0.000
 EP-M LIM1 0.000
 PH LIM2 14.000
 0106

ROUTINE # 201
 REAGENT 0,05 n NaOH wBr.
 TITER 1,000
 ELECTRODES 2 kombinierte Glaselektrode Metrohm,
 geeicht.

SAMPLE 1672,3 mg LP 1845, Thiohol

REMARKS SÄurebestimmung

Fig. 6:

Analysis of LP 1845: Determination of free nitric acid : titration curve (top) and 1st derivative (bottom)

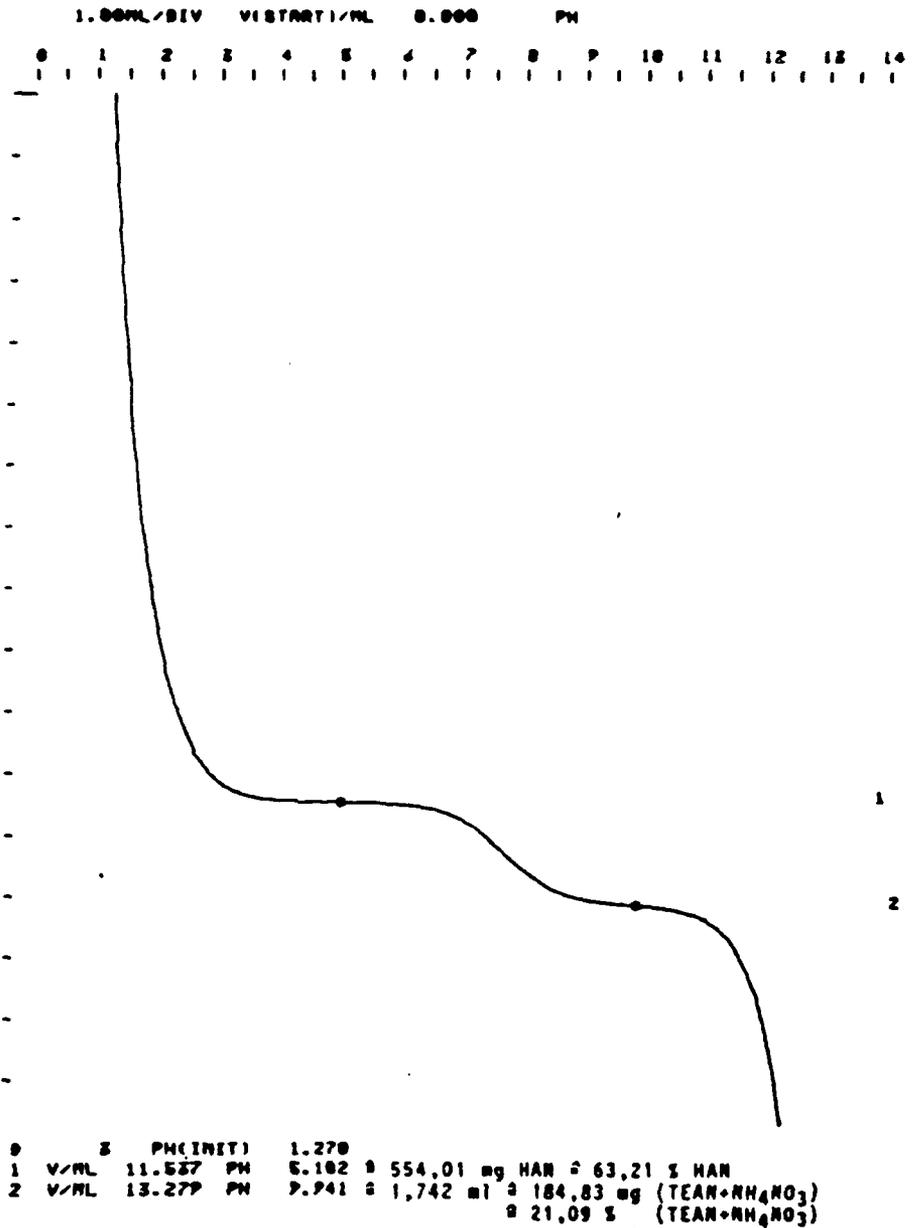


Fig. 7: Analysis of LP 1845: Simultaneous determination of HAN and TEAN by substitution titration: Titration curve. Here: 1) Determination of HAN after acetoxim formation by the addition of acetone
 2) Determination of TEAN

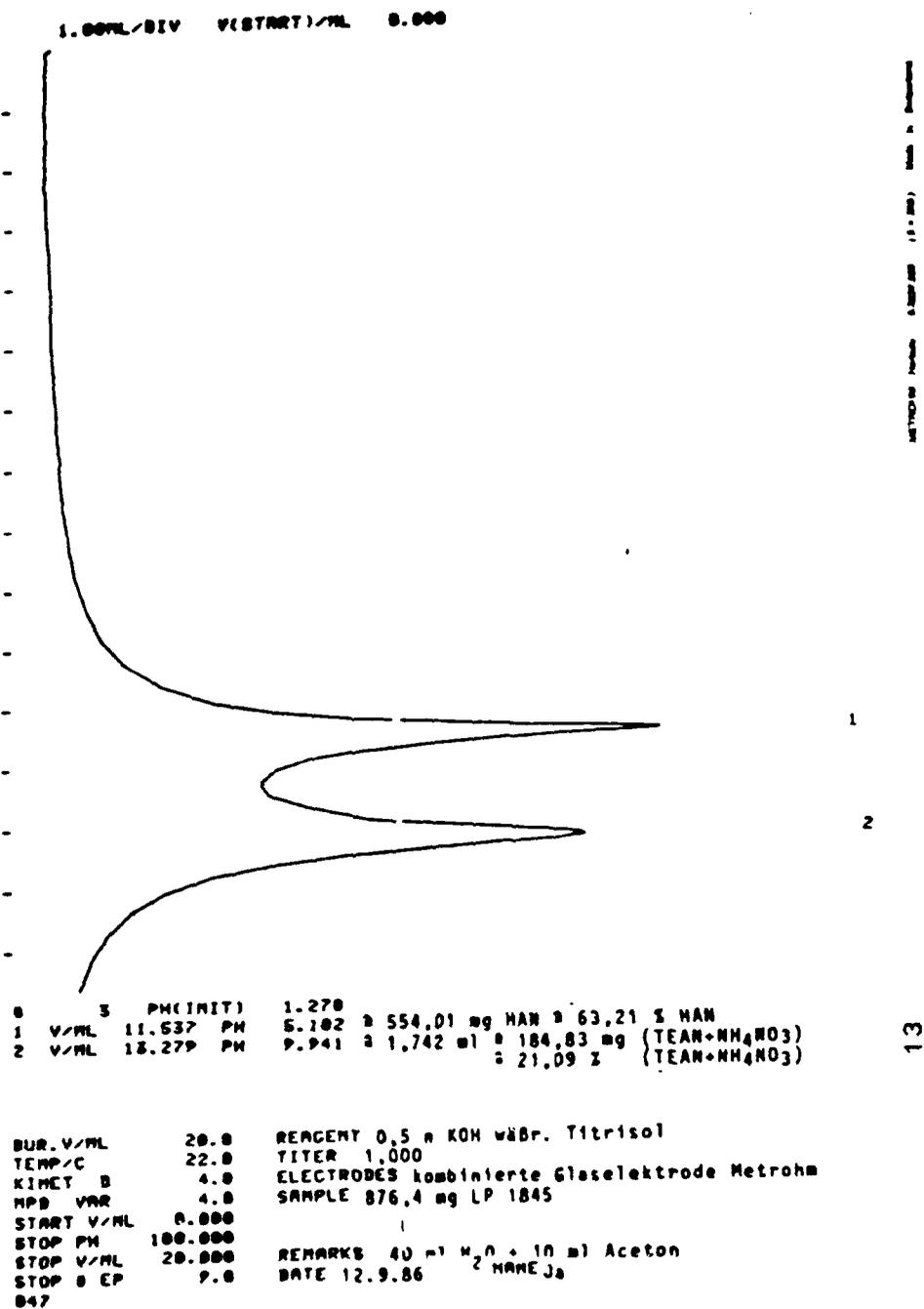


Fig. 7.1: Analysis of LP 1845: Simultaneous determination of HAN and TEAN by substitution titration: 1st derivative. Here: 1) Determination of HAN after acetoxim formation by the addition of acetone
 2) Determination of TEAN

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