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HISTORICAL AND EXPERIMENTAL STUDIES OF ALKALI AND TRINITROTOLUENE REACTION

NAVAL WEAPONS SUPPORT CENTER

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HISTORICAL AND EXPERIMENTAL STUDIES OF ALKALI AND TRINITROTOLUENE REACTION

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DEPARTMENT OF THE NAVY
SEA SYSTEMS COMMAND

PREPARED BY

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Reaction of aromatic nitro compounds with alkali is reviewed in the literature as far back as 1886. Studies of the reaction of trinitrotoluene and aqueous alkali were conducted in the laboratory. Various analytical techniques such as infrared spectrophotometry, uv-visible spectrophotometry, liquid chromatography, thin layer chromatography and atomic absorption

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spectrophotometry were used in the structure investigations. Direct structural identification of the reaction products with the methods employed was not possible; however, enough evidence was available to allow the proposal of a possible structure for the material formed in the reaction. Evidence points to the presence of TNT anion and a Janovsky complex being formed early in the reaction. Nitrite liberation indicates the possible formation of a charged dinitro quinoid ion. Final products are postulated as mono, di and tripotassium nitronate salts of toluene.

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Historical and Experimental Studies of Alkali and Trinitrotoluene Reaction

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6 October 1975

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SUMMARY

The purpose of this study is two-fold. The first is to review the literature on the reaction of alkali with 2, 4, 6-trinitrotoluene, including the reactions of nitro substituted aromatic components in general and their reaction with basic materials. Comparisons and differences between the reactions of trinitrotoluene and the reactions of other nitro substituted aromatic compounds are discussed in the review.

The other purpose is to conduct experiments in the laboratory to study the reactions of trinitrotoluene in aqueous alkaline solutions. A comparison between the reactions in aqueous media observed experimentally and the reactions in mixed aqueous or nonaqueous media reported in the literature is made. The material formed from the alkali-trinitrotoluene reaction was isolated and studied by various analytical techniques. Direct structural identification of the reaction product with the methods employed was not possible; however enough evidence was available to allow the proposal of a possible structure for the material formed in the reaction. Evidence points to the presence of TNT anion and a Janovsky complex being formed early in the reaction. Nitrite liberation indicates the possible formation of a charged dinitro quinoid ion. Final products are postulated as mono, di and tripotassium nitronate salts of toluene.

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NOMENCLATURE

Throughout this thesis it will be necessary to refer to 2,4,6-trinitrotoluene and the designation "TNT" will always refer to this particular isomer of trinitrotoluene. The term "red TNT" will always refer to the colored product or products formed from the reaction of alkali and TNT in water or alcohol-water media. Other designations, such as "Meisenheimer complex", will be explained in the body of the thesis.

I. INTRODUCTION

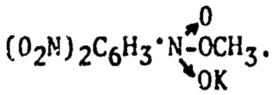
Red TNT is produced in aqueous or alcoholic-aqueous media when TNT is reacted with alkali. The aqueous system is of interest because waste water from defense plants often contains red TNT, as evidenced by its red color. A knowledge of the properties of red TNT will be beneficial for water pollution studies. Studies of the properties and possible structure of the material dubbed "red TNT" will therefore be made.

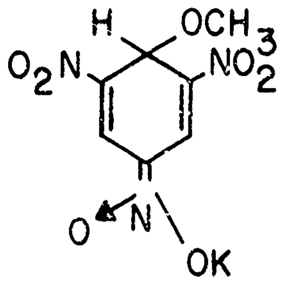
Of importance are questions such as the following: Does red TNT consist of one or more components? Can red TNT be formed under different conditions? Once red TNT is formed, how does it act under varying pH conditions? What materials will adsorb the red TNT? The answers to these questions can be of value when studying the effects of TNT in water pollution.

It is desirable as a background to this study to review the literature regarding the reaction of basic materials with TNT and to draw together in one place a review of past work and the conclusions that were drawn therefrom.

II. HISTORICAL BACKGROUND

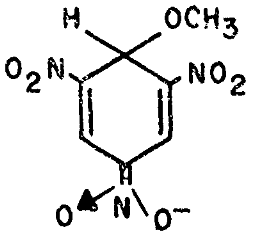
References to the reaction of nitro compounds with alkali go back as far as 1889[1]. Meisenheimer[2] and Hantzsch[3] published articles on this subject about the turn of the century. Their studies were conducted in alkaline alcoholic media, as were the majority of studies reported on this subject up to the present time.

Hantzsch and Kissel[4] reacted potassium hydroxide and methyl alcohol with TNT to get an addition compound of TNT and methyl alcohol which is the nitronic acid from which the alkali metal salts are derived. Hantzsch[4] originally suggested that the addition took place on one of the nitrogen atoms of a nitro group and wrote the potassium salt of trinitrobenzene as  $(O_2N)_2C_6H_3\cdot\overset{\nearrow O}{\underset{\nwarrow OK}{N}}\text{-}OCH_3$. Meisenheimer[2] disagreed because the accompanying color change observed in the reaction suggested to him that the aromatic ring was involved. He suggested attachment to a carbon atom in the ring instead of to a nitrogen atom. His proposed structure was (1).



1

He found supporting evidence by experimentation. No real explanation of the color formation was offered. The fact that more than one nitro group is required for this type of salt formation was not alluded to either. Urbanski[5] suggests that the stability and color of these salts indicate involvement of all the nitro groups. He shows the involvement of the nitro groups by writing the anion of the addition product of potassium methylate and trinitrobenzene in three forms, as shown in structures (2), (3) and (4):



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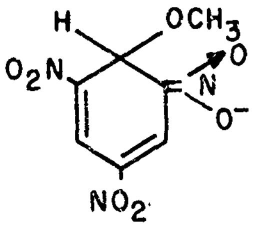

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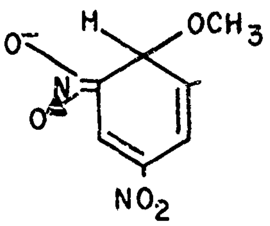

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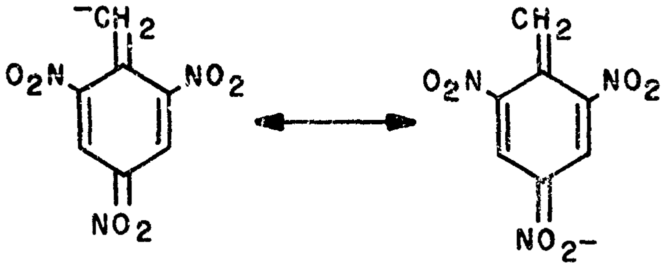
The anion is probably a resonance hybrid of all three forms and would therefore be a stable structure. Urbanski[6] further states that the color may be due to the resonance of the anion between the quinonoid systems.

Urbanski[7] also discusses reactions of unsymmetrical isomers of trinitrotoluene. Aqueous solutions of sodium or potassium hydroxide form the corresponding salts of dinitrocresol. The nitro group in the meta position to the methyl group is quite mobile. Likewise, a nitro group ortho or para to other nitro groups is also mobile and can easily be displaced by other substituents. Therefore the products of these reactions are well characterized.

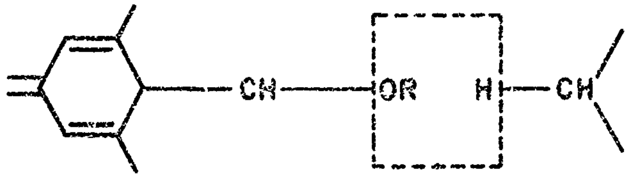
Caldin and Long[8] state that the reaction of TNT with ethoxide appears to be a proton transfer which produces a colored anion. They suggest that the rate of the ethoxide-TNT reaction may be controlled not only by proton transfer but also by accompanying changes such as the movement of solvent molecules. They do not rule out the possibility of the ethoxide-TNT reaction being an addition reaction. They offer experimental evidence that favors proton transfer and attribute the stability of the TNT anion to a resonance structure shown as (5) and (6).



5 6

This shows a delocalization of the negative charge over the whole molecule. When a nitro group conjugates with the π electrons of the benzene ring as in structure (6), the group must be coplanar with the ring. A methyl group ortho to the nitro group will oppose this arrangement, so that the contribution of structure (6) will be reduced along with its stability.

Muller[9] discusses the formation of quinol nitrol acids. The colored compounds formed by nitro-substituted aromatic compounds in alcoholic alkaline media occur only when one or more free hydrogen atoms are present in the nitro compound. The free hydrogen atom must be associated with nuclei that are not substituted. Zimmermann[10] proved that the alkali salts of quinol nitrol acids react with the highly mobile hydrogen atom of the methylene component, accompanied by condensation, in accordance with the model (7).



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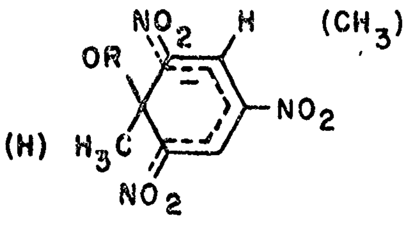
The example of m-dinitrobenzene is cited. It will initially remain colorless with aqueous-alcoholic alkali. When a component is added whose carbon is bonded to active hydrogen atoms, an intensive pigmentation takes place immediately. The reactions giving pigmented products in the "xylol musk" was attributed to the hydrogen atoms of the methyl group attached to the ring.

Bernasconi[11] also discusses Caldin and Long's[8] 2, 4, 6-trinitrobenzyl anion (TNT^-) formation from TNT and strong base. Although Servis[12] argues against TNT anion formation, Crampton[13] concludes the "present evidence suggests, on balance, that the violet color produced in alcoholic media is due to TNT anion, though adducts formed by the addition of alkoxide ion, or the TNT^- itself, to TNT may be produced in some circumstances." Bernasconi also mentions Ainscough and Caldin's[14] studies of the TNT and ethoxide ion reaction in ethanol at high base concentrations. This interaction was attributed to a charge transfer complex, although a Meisenheimer complex could not be excluded. Like other investigators, Bernasconi's studies were conducted in methanol or ethanol solutions of alkali. His aqueous system was 50% dioxane-50% water. Some spectral studies were conducted in 10% dioxane-90% water.

Bernasconi[11] also studied reaction rates in the alcohol and dioxane systems. The presence of three processes were detected and he measured the relaxation times of these processes. Relaxation describes the self-adjustment of a perturbed molecular system to its equilibrium. The initial kinetic process was so short that only an estimate of 0.4 to 2.0 milliseconds for the relaxation times could be made in methanol. The second and third processes occured in 0.3 to 1 second and 10 to 30 milliseconds, respectively. The kinetic process times were given for ethanol and dioxane systems too. The concentrations of TNT and alkoxide (hydroxide for dioxane system) were varied to show the dependence of each kinetic process on concentration. Reaction schemes are presented for the three systems. He favors the formation of a Meisenheimer complex (8) for the initial rapid process, and concludes that the second process involves the formation of TNT^-, while the third process is reaction of TNT and TNT^- to form a Janovsky complex (9).



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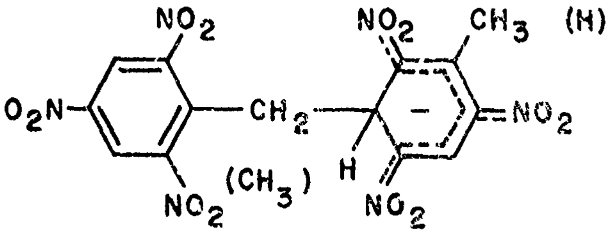

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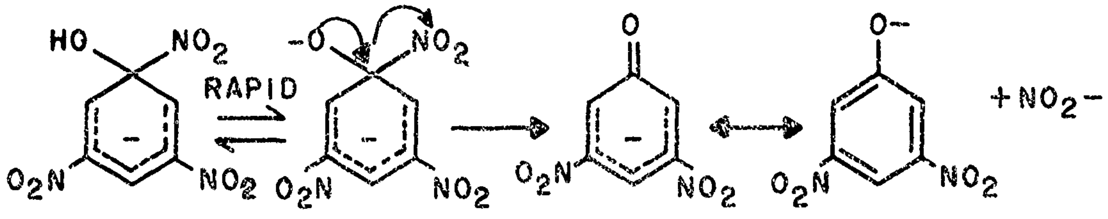
The Janovsky[15] reaction itself is the interaction of nitro substituted aromatic compounds with ketones in basic ketone-water solutions. Bernasconi presents data that support the reaction scheme. UV-visible spectra presented for TNT^- were obtained by calculation from spectra of TNT solutions in excess base and kinetically determined equilibrium data. The spectrum obtained for basic TNT in 10% dioxane-90% water was quite different from that in the other three systems. He concludes that if TNT^- is formed at all, it is a very transient species. The species formed has not yet been identified. He presents a uv-visible spectrum of the Janovsky complex from calculations. His findings show that as the water content decreases the TNT^- species becomes the major component.

Bernasconi and Bergstrom[16] carried out similar studies with 1, 3, 5 trinitrobenzene. The studies were conducted in approximately 80-20 water-alcohol mixtures. They observed that going from either pure methanol or ethanol to the corresponding aqueous solutions had a small retarding effect on the rate of attack by MeO^- and EtO^-.

Norris[17] reports that sodium sulfite reacts with 1, 3, 5-trinitrobenzene, TNT and 2, 4, 6-trinitrobenzaldehyde in aqueous solution to form a 1:1 complex with absorption maxima at 462, 465 and 458 millimicrons, respectively.

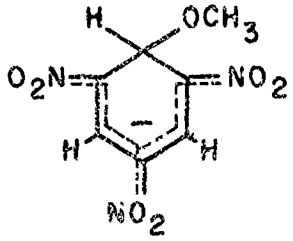
Numerous articles have been published on the effects of visible and UV radiation on nitro substituted aromatic compounds. Investigators Krauz and Koci[18] report the formation of trinitrobenzoic acid and picric acid from action of ultraviolet rays on TNT. Gold and Rochester[19] mention the photochemical hydrolysis of 1, 3, 5-trinitrobenzene in alkaline media. They note that the loss of a nitro group (as nitrite ion) and conversion of trinitrobenzene to 3, 5-dinitrophenoxide ion is accelerated by light. Their studies showed that the photochemical effect does not extend over the entire visible region. They state that a hydroxyl group attaches to a site occupied by a nitro group in the trinitrobenzene charged ion and then a nitro group leaves as a nitrite ion. This is shown in the sequence (10), (11), (12) and (13).



10 11 12 13

Their conclusion that a hydroxyl group does not leave more readily than a nitro group is based on observations of nitro group replacement in trinitrobenzene by methoxide as being a fairly rapid reaction. They say methoxide is therefore not favored relative to nitrite. The hydroxyl group is eliminated from similar structures less rapidly than alkoxide group, so it follows that the hydroxyl group would not be expected to leave more readily than the nitrite group.

According to Hall and Poranski[20], modern techniques and theory have shown that four types of interaction of bases with polynitroaromatics exist, giving rise to charge-transfer complexes. They are: (1) addition of one or more molecules of the base to the nitro substituted aromatic ring; (2) abstraction of a proton from the nucleus or from one of the substituents of the nitro compound; (3) transfer of an electron from the base to the polynitroaromatic compound, resulting in the formation of radical anions; and (4) formation of a donor-acceptor complex between neutral molecules as defined by Briegleb[21]. Crampton and Gold's[22] nuclear magnetic resonance studies indicated the anion (14) to be present for the monopotassium methoxide complex of 1, 3, 5-trinitrobenzene in dimethyl sulfoxide.



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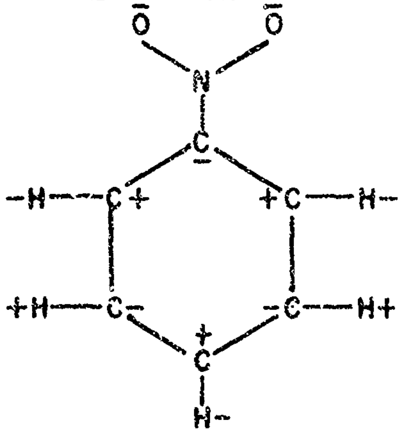
Problems involved with using electronic spectra for identification of species in basic polynitroaromatic solutions were enumerated[20]. Spectrophotometric measurement of absorptivities is used to establish the thermodynamic quantities of the reactions involved. The reactivity of polynitroaromatics poses problems. The reactant or product can decompose and some of the reactions are light catalyzed. Changes in spectra with time or with base concentration are very hard to detect because of similarity of spectra for the different species present. If a reaction goes through a series of reaction products, then extinction coefficients will be in error because of possible band shifts. The slow reaction of TNT with alkoxides and other bases was alluded to as a controversial subject. In the first place alkoxide solutions of TNT are not stable at room temperature. The major species formed in the reaction has not been identified by such methods as nuclear magnetic resonance spectroscopy. Some nuclear magnetic resonance studies have shown rapid exchange of methyl hydrogens with deuterium from CH_3OD in a particular solvent system and this has been verified by mass spectroscopy. Hall and Poranski[20] mention that most authors apparently assume that reaction of base with polynitroaromatics in aqueous solution is analogous to the reaction in methanolic solution. A table containing wavelengths of absorption maxima of di and tri-nitroaromatics in water is presented. The initial product formed with TNT in water gave a maximum at 515 millimicrons. A further product gave maxima at 470 (the strongest) and at 530 millimicrons. The isosbestic wavelengths were 495 and 540 millimicrons. Under Janovsky conditions TNT gave absorption maxima at 460 and 500-530 millimicrons.

In discussing ultraviolet absorption spectra of nitro-substituted benzenes Abe[23] mentions that aqueous solutions of sodium hydroxide with nitro compounds show intense absorption bands at longer wavelengths in the order of increasing number of nitro groups. He says the color of the nitro compounds with sodium hydroxide seems to be produced by the formation of complexes between the compounds and the hydroxide ion. This is understood because the compounds give the same color with other alkalies and the position of the absorption maxima of nitro compounds in water are not influenced by the concentration of excess strong acid.

Urbanski[24] has discussed the directing effects of the nitro group. Nitration is due to a positive ion NO_2^+. Nitration by ionic substitution or displacement is an electrophilic substitution. He mentions that meta-directing groups such as NO_2 are acidic, whereas basic (NH_2) or neutral groups (CH_3) are ortho- and para-directing. This rule was given by Noelting[25]; however, there are exceptions, such as a phenolic OH group which is ortho - para-directing although it should be considered acidic. A table of directing powers of various groups was given. An example was given which compares the directive powers of the nitro group and the methyl group, even though one is meta-directing (NO_2) while the other is ortho - para-directing (CH_3). The example is the further nitration of meta-nitrotoluene and in this reaction the nitro group enters the ortho and para positions relative to the methyl group. It follows from this experiment that the directive effect of the nitro group is less than that of the methyl group. Urbanski[24] refers to Fry's[26] suggestion of distribution of charges in an aromatic ring with a meta-directing or ortho - para-directing group present. A meta-directing group such as nitro induces a positive charge on the hydrogens in the meta position. The nitro group is electron withdrawing (attracting) in nature. An ortho - para-directing group (Cl-, CH_3-) induces positive charges at the hydrogen atoms in the ortho and para positions. Fry further says that positively charged hydrogens are readily substituted. The charges on the benzene ring, according to Fry, are shown as (15) and (16).



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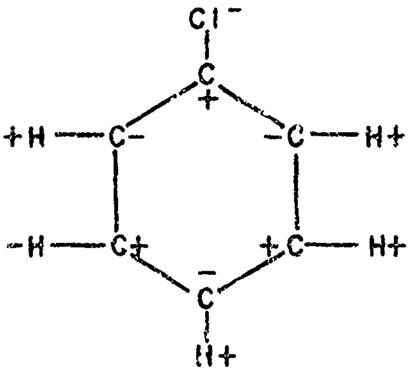

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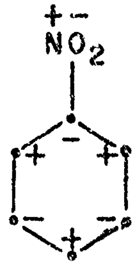
Vorlander[27] showed the difference between meta - and ortho - para-directing substituents by structures (17) and (18).



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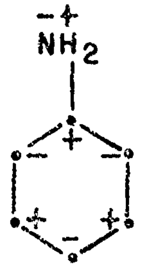

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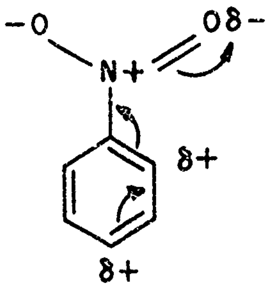
Titov[28] classifies all substituents into two catagories: first, those facilitating the oxidation of the benzene ring to the quinonoid one and, second, those inhibiting the formation of the quinonoid system. Electron donating groups (CH_3) which are ortho - para-directing belong to the first class while electron attracting groups (NO_2) which are meta-directing belong to the second class.

Urbanski[24] states that Fry[26] and Vorlander's[27] concepts are precursors of the modern electronic interpretation. The importance of a key atom in a directing group was discussed. The more polar characteristics the key atom has, the more the substitution is restricted to one type. The methyl group in toluene favors ortho - para substitution, but meta substitution is known to exist to the extent of 4%. This is explained by a very weak electronegativity of the carbon atom and very weak electropositivity of the hydrogen atoms in the methyl group. Terminology was developed for an electrophilic group such as the nitro group producing a negative inductive effect "-I". Conversely, nucleophilic substituents are represented by "+I" (positive inductive effect). The concept of mesomeric effect "M" was introduced as well. The mesomeric effect (negative for nitro) is considered a form of permanent displacement of charge. Applying this terminology the nitro group is electron withdrawing through both its -I effect (reduced electron density at each nuclear carbon) and -M effect, which causes further electron withdrawal from ortho and para positions. An isolated molecule containing a nitro group would appear as (19) using this terminology:

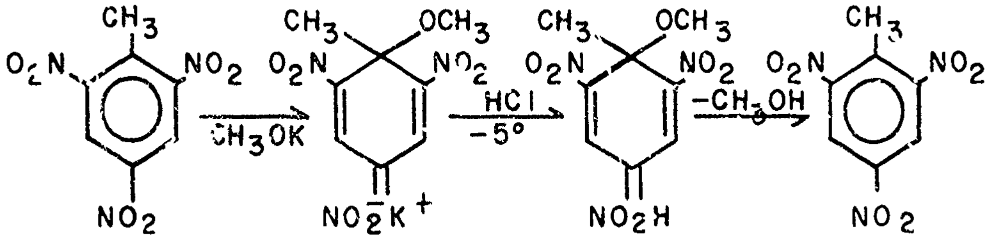


19

Norman and Radda[29] point out that the methyl group acts contrary to the nitro group in nitrotoluenes. When electrophilic substitution takes place in nitrotoluene, the electron - donating methyl group acts contrary to the nitro group. The nitro group destabilizes in the order meta < ortho < para, whereas the methyl group stabilizes in the same order.

Rao[30] discusses the infrared spectral characteristics of nitro substituted aromatic compounds. Coplanar aromatic nitro groups generally show asymmetrical stretching vibrations in the region 1520 - 1550 cm^{-1}. If strongly electron withdrawing groups in the para - position or bulky groups in the ortho - position are present, then the asymmetric frequency tends to increase to 1540 - 1570 cm^{-1}. Electron donating groups lower the frequency to 1490 - 1525 cm^{-1}. The stretching bands of the nitro group are very strong, but it is not possible to estimate number of nitro groups by these bands due to variability of intensities from one compound to another. Generally the asymmetric stretching band is much stronger than the symmetric stretching band. Steric hindrance causes band shape changes. Covalent nitrates show asymmetric stretching at 1600 - 1650 cm^{-1} for the nitro group. The symmetric stretching vibration occurs at 1250 - 1300 cm^{-1}. Sodium salts of nitroalkanes show asymmetric and symmetric stretching frequencies at 1200 - 1320 cm^{-1} and 1040 - 1175 cm^{-1} respectively. The C = N frequency in these salts occurs at 1585 - 1605 cm^{-1}.

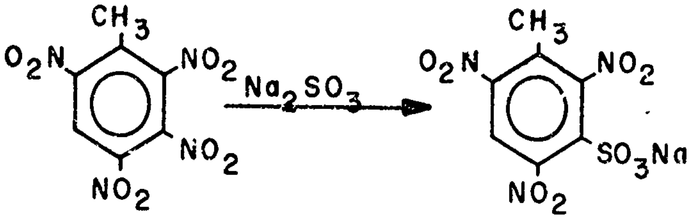
Nielson[31] discusses the infrared spectra of nitronic acids, esters and salts. The C = N absorption for nitronic acids occurs near 1620 - 1680 cm^{-1}. The nitronic esters absorb strongly in the region 1610 - 1660 cm^{-1} (C = N). The C = N absorption for nitronate salts occurs at 1587 - 1605 cm^{-1}. For the OH band the nitronic acid stretching region resembles that of carboxylic acids. No free OH band is present. The broad OH envelope occurs in the 2500 - 3000 cm^{-1} region. Aliphatic nitronic acid spectra in the ultraviolet are discussed. A strong band is found at 220 - 230 millimicrons when measured in ethanol or water. The nitronate anions absorb about 10 millimicrons higher. The nitronic acid of mononitrobenzene gives maxima at 284 millimicrons in water. The corresponding sodium salt absorbs at 294 millimicrons. Nielson gives the following reaction of TNT (20) with potassium methoxide followed by acidification:



20 21 22 20

Usually upon acidification of the Meisenheimer - type salt the nitro substituted aromatic compound is produced because of the instability of the nitronic acid.

J. de Boer and I. P. Dirkx[32] explored the activating effects of the nitro group in aromatic substitutions. They discussed the activation and displacement of a nitro group by suitable electron withdrawing substituents. Sterically hindered nitro groups are displaced smoothly even at low temperatures. The purification of TNT by reaction with sodium sulfite was given as an example. Unsymmetrical polynitro compounds (23) are removed as soluble sulphonates (24). The mobility of the nitro groups due to overcrowding is considerable. This removal of the nitro group is



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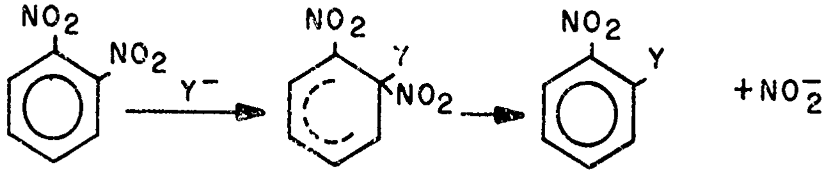
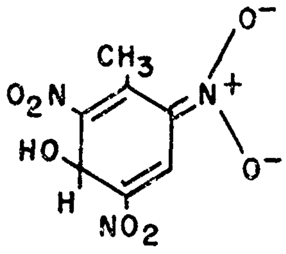
facilitated by activation of the nitro groups by another electron withdrawing substituent. With hydroxide and alkoxide ions the nitro group is displaced but slowly at room temperature, as the sequence (25), (26) and (27) shows.



$Y^- = OR^-, NH_2^-, SAr^-, SO_3Na^-$

25 26 27

Although Rosenblatt, Lauterbach and Davis[33] were mainly concerned with preventing water pollution resulting from TNT manufacture, they make reference to and discuss products formed from the TNT - base reaction. While discussing the Seilite process which removes undesirable TNT isomers by reaction with sodium sulfite, they mention "a typical Meisenheimer complex" (28) which is formed between sodium hydroxide and TNT.



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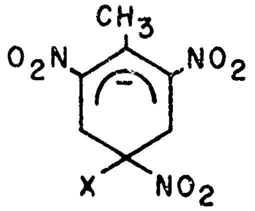
The photochemistry of TNT was also discussed by these authors and several references on the subject were cited. An intermediate compound with the formula $(NO_2)_3C_6H_2 - CH_2OH$ has been isolated. An uncharacterized water soluble red dye is formed. Conclusions were drawn from the literature that an excited state intermediate of the type (29) might be favored in photochemical



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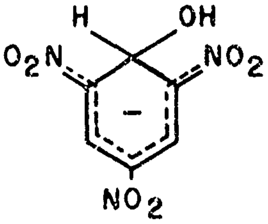
reactions of TNT. A weak nucleophile can attack the polynitro compound causing loss of X^-, NO_2^- or even hydride. Photochemical reaction of nitro substituted aromatics in nucleophilic media results in loss of nitrite ion. If nitrite is not displaced, then the displaced group comes from the position meta to the nitro groups. Nucleophilic displacement reactions were discussed as applied to removal of unwanted isomers of dinitrotoluene (DNT) from the desired isomers of DNT and 2, 4, 6-trinitrotoluene. Through these mechanisms there are products formed that are water soluble and are highly colored even at low concentrations. The authors state that a variety of colored compounds are formed from reaction of bases with polynitroaromatics. The identification by Bernasconi[34] of the reaction of amines with 1, 3, 5-trinitrobenzene was given as an example. One of the materials of particular interest was the Meisenheimer complex (30).



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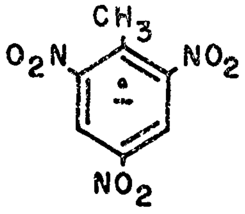
Numerous structures for the colored species have been postulated. Of particular interest is (31) which is an anion radical produced by complete charge transfer. Also mentioned was the ion of structure (5), which was postulated by Caldin and Long[8] and later by Bernasconi[11], who gives evidence for its existence. This anion is most probably generated in strongly basic solution.

The activating effect of the nitro group on the aromatic ring during nucleophilic substitution reactions depends on the position of the displaced substituent relative to the nitro group. The nitro group's effect on the ortho position is stronger than on the para position unless steric factors enter in. Although the effect on the meta position is much less than the ortho and para effects, activation is still present. Other substituents may retard or accelerate the reaction provided they are sterically remote from the reaction site. Two meta nitro groups activate 1.8 times as much as a single para nitro group according to de Boer and Dirkx[32].



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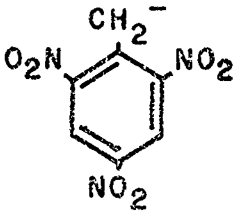

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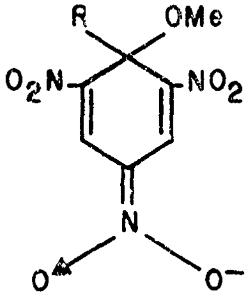
In discussing aromatic nucleophilic substitution, Bunnett[35] states that the nitro group accepts electrons by mesomeric interaction and generally activates equally from the ortho and para positions. Coplanarity with the ring is required for the maximum activating effect. Their effect is reduced when a bulky substituent is ortho to the nitro group.

Ainscough and Caldin[36] discuss the reaction of sodium ethoxide with 2, 4, 6-trinitroanisole, 1, 3, 5-trinitrobenzene and TNT in ethanol. UV and visible spectral studies were made. Concentrated solutions of TNT in sodium ethoxide show an initial reaction which rapidly produces a brown solution, passing slowly over into the usual purple. Evidence shows the purple species is an anion derived from TNT by loss of a proton. It has been postulated that the brown species is an addition compound of TNT with ethoxide. This compound could be either a charge-transfer complex or an addition compound like Meisenheimer[2] described.

Farmer[37] says the reaction of alcoholic alkali with trinitrobenzene produces colored compounds that are quinonoid in nature. The products contain two nitro groups, a nitronate group and two gem - substituents, one of these being an alkoxy group.

According to Meisenheimer[2] a trinitrobenzene derivative, $(NO_2)_3C_6H_2R$, reacts with potassium methoxide to form a quinonoid nitronate ion in which the substituent R and a methoxy group are attached as shown (32):



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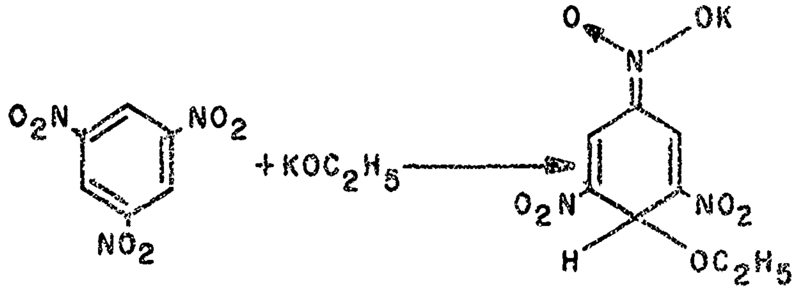
The anion has been assumed to be a resonance - hybrid of the ortho - and the para - quinonoid form.

Karrer[38] discusses the reactions between nitro substituted aromatic compounds and alkalies. He likens the nitro substituted aromatic compound to tertiary aliphatic nitro compounds because the carbon to which the nitro group is attached has no hydrogen atom. He says the nitro substituted aromatic compound cannot form alkali salts since the aci-form is not possible. Nitro substituted aromatic compounds therefore do not dissolve in alkalies. He then turns around and says many nitro substituted aromatic compounds (33) can add on the alkali alcoholates. Colored salts are produced with the probable constitution of (34).



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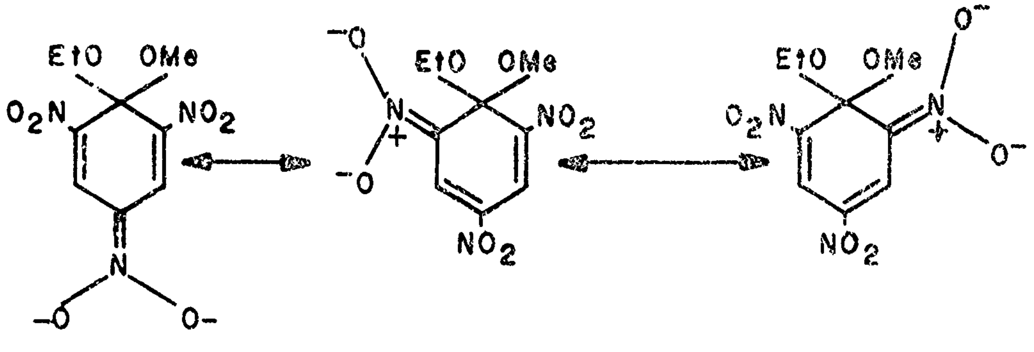
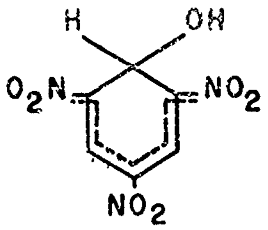
Sidgwick[39] also discusses the colored materials formed between trinitroaromatics and alkoxides. He gives the differing views of Hantzsch[4] and Meisenheimer[2]. Meisenheimer does not explain why more than one nitro group is required for colored compound formation. Sidgwick says it is evident that all the nitro groups have something to do with the color and stability. The compounds that form the salts have two or more nitro groups present in meta positions to each other. The anion he considers is shown in mesomeric structure as (35), (36) and (37).



35 36 37

There is no steric inhibition because the alkoxy groups lie above and below the plane of the ring. Such a structure accounts for necessity of more than one nitro group; resonance stabilization resulting from mesomerism compensates for loss in resonance stabilization suffered by the ring.

Bernasconi[40] has extensively studied intermediates in nucleophilic aromatic substitutions. He has conducted studies with excess aqueous sodium hydroxide and trinitrobenzene. The same complex that was previously mentioned (30) was formed.



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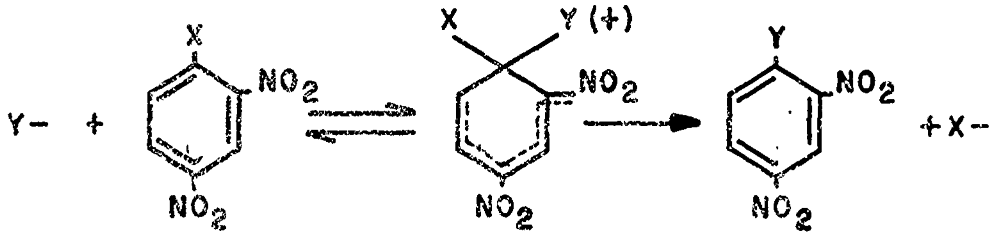
Bernasconi[41] says the stability of Meisenheimer complexes is affected by the aromatic residue, the attacking nucleophile, the leaving group and the solvent. He says the stability increases with any feature in the aromatic residue which brings about a more efficient delocalization of the negative charge with increasing carbon basicity of nucleophile and leaving group, with decreasing polarity and hydrogen bond donating ability of the solvent as long as anionic nucleophiles are involved. Bernasconi[34] states that the main feature in activated nucleophilic aromatic substitution reactions is that the nucleophile attacks the aromatic substrate (38). Generally, activation occurs from one or several nitro or other electron-withdrawing groups to form a high-energy intermediate (39), often referred to as a Meisenheimer Complex (MC), which can either proceed to products (40) in a second step or revert to reactants (38), as below:



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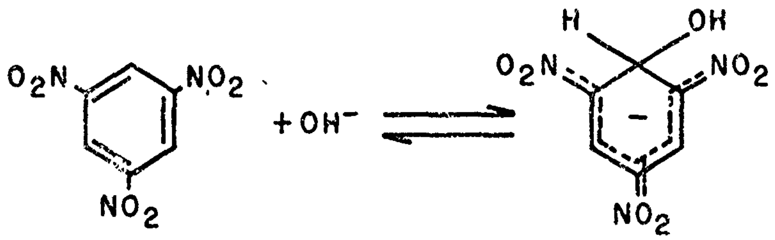
Previous comments (page 16, this thesis) on this showed Y^- as OR^-, NH_2^-, SAr^- and SO_3Na^-; X was another nitro group which left as nitrite ion. Bernasconi[34] mentions a red color appearing immediately after mixing trinitrobenzene with aliphatic amines in a variety of solvents. This is generally attributed to MC. Although the article deals with amine reactions with trinitrobenzene (33), he mentions a reaction which does not depend on amine concentration or pH below 12. The reaction is:



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Russell and Janzen[42] dealt with the reaction of nitrotoluenes with t-butyl alcohol containing potassium t-butoxide, but make some statements about TNT. They say that TNT is one of several highly acidic p-nitrotoluene derivatives that fail to produce radical anions in the presence of either deficient or excess base. In excess base it might have been expected that these derivatives would be converted to their anions so rapidly that electron transfer could not be observed. The absence of electron transfer in the presence of deficient base clearly shows that the nitroaromatic nucleus is incapable of oxidizing these polynitro-stabilized anions.

Foster and Hammick[43] present infrared spectrophotometric data on potassium ethyl 1-methoxypicrate. Although this does not concern TNT, it may show an expected trend in behavior of absorption bands. The starting compound was s-trinitroanisole (TNA). The N-O symmetrical stretching frequencies appear to have shifted from 1343 cm^{-1} in TNA to 1291 cm^{-1} in the product formed from TNA and potassium ethoxide. The N-O asymmetrical stretching frequencies have shifted from 1552 to 1492 cm^{-1}. These bands have been assigned 1349 ± 9 and 1518 ± 13 cm^{-1}, respectively. The aromatic C-H stretching frequency at 3000-3090 cm^{-1} is absent. Sidgwick[44] suggested that these differences are due to an increased negative charge on the nitro groups.

Buncel, Norris, and Russell[45] mention the interaction of nitro substituted aromatic compounds with a variety of bases. Brightly colored solutions are produced. They discuss the theory of transfer processes and give experimental results. A partial transfer (through orbital overlap) of electronic charge from the base (Y: of Y^-) to the aromatic nucleus depleted of π-electron density, owing to the electronegative nitro substituents, gives rise to π-complexes, also known as donor-acceptor or charge-transfer complexes. A further degree of interaction may lead to an electron from Y^- becoming completely transferred to the nitro compound, in which case a radical-anion is produced.

In contrast to electron-transfer processes is the interaction by which the unshared electron pair of Y^- is used in the formation of a covalent bond to an aromatic carbon atom. The resulting species is then a σ-complex and will no longer have the benzenoid resonance intact. The best known of such σ-complexes is the red 'Meisenheimer adduct' ($Y=OCH_3$) formed from 2, 4, 6-trinitroanisole and methoxide ion in methanol. If the nitro substituted aromatic compound contains a displaceable group (halogen), then the base may act as a nucleophile and we enter the area of nucleophilic aromatic substitution. As a further possible interaction, the basic reagent may take part in proton-abstraction processes. This possibility arises owing to the powerful electron-withdrawing capability of nitro groups, which may cause a hydrogen atom of the nitro substituted aromatic compound to become sufficiently acidic. Abstraction of a nuclear hydrogen would yield an aryl carbanion, while abstraction of a hydrogen bound to an alpha carbon atom would give rise to a nitrobenzyl anion.

Because of similarities of the visible absorption spectra of 1, 3, 5-trinitrobenzene-ethoxide ion and 2, 4, 6-trinitrobenzene-ethoxide ion complexes in solution, the former was formulated as a σ -complex in which the ethoxide ion is covalently bonded to a ring carbon atom and the negative charge is shared among the three nitro groups.

For 1-substituted 2, 4, 6-trinitrobenzenes, complex formation may occur at both the 1- and the 3- position either preferentially or simultaneously, and the absorption spectra of the two complexes may differ appreciably. In the interaction of 2, 4, 6-trinitroanisole with methoxide ion, attack occurs first at the 3-position though the final product of the reaction contains methoxide ion in the 1-position.

Ultraviolet-visible absorption results so far on the interaction of nitro substituted aromatic compounds with anions (basic) suggest the formation of σ -and Meisenheimer complexes.

The reaction of 1-substituted 2, 4, 6-trinitrobenzenes with bases is slightly more involved, as either a σ -complex of the general type suggested by Meisenheimer or a σ -complex formed by attack at C may be obtained. If, in addition, the substituent contains one or more acidic protons, ionization to the conjugate base may occur in competition with σ -complex formation and the conjugate base may itself undergo anion attack. Attack of the base at a carbon containing a nitro group is not considered to be a likely process.

The possibility of the occurrence of nuclear hydrogen abstraction in the interaction of nitro substituted aromatic compounds with bases first arose in connection with the observations that solutions of some nitro substituted aromatic compounds in amines, and in liquid ammonia are conducting.

The introduction of nitro groups into the aromatic ring of toluene and its derivatives increases their Bronsted acid strength, so that in sufficiently basic solution it is possible to remove a proton to produce substituted benzyl anions. Caldin and Long[46] have shown TNT gives a purple anion with sodium ethoxide in ethanol. The maxima are at 510 and 370 millimicrons. They note picrate ion in methanol has maxima close to 370 millimicrons and conclude that the 2, 4, 6-trinitrobenzyl anion (TNT^-) is formed.

$$TNT + OEt^- \qquad\qquad TNT^- + HOEt$$

The large positive entropy change in this reaction in ethanol solution is interpreted by Caldin as being due to the desolvation which occurs when the ethoxide ion, with its charge localized mainly on the oxygen, is replaced by the trinitrobenzyl anion in which the charge is delocalized. A significant part of this desolvation appears to occur in the formation of the transition state because the entropy of activation is positive.

III. EXPERIMENTAL STUDIES

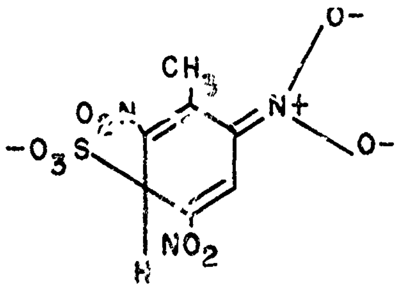
A. Initial Considerations

Early experiments showed that red TNT could be formed from reaction of TNT - water solution with any of the following materials: sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium carbonate, sodium hydrogen carbonate, and sodium sulfite.

Ammonium hydroxide was not used because it would not be present in the waste water from TNT manufacturing operations or bomb steam-out facilities. In addition, it is desirable to watch for ammonia evolution, if any, in base - TNT reactions.

The carbonate salts were not considered after laboratory studies indicated that the only two solvents that dissolved red TNT significantly also dissolved the carbonate salts, i. e., water and methanol. Infrared spectra of products from carbonate solutions tended to show carbonate with no significant appearance of organic bands due to red TNT. Concentrated solutions of alkali hydroxides used for the purpose of forming red TNT gave the same problem of carbonate contamination in the infrared spectra, as will be elaborated on later.

Sodium sulfite is a likely candidate for studies of its reaction with TNT in water solution. These studies have already been made to some extent. During the manufacture of TNT, sodium sulfite is used to remove unwanted isomers of TNT (Sellite process)[33]. The reaction of sodium sulfite with TNT is slow and forms addition compounds such as (41).



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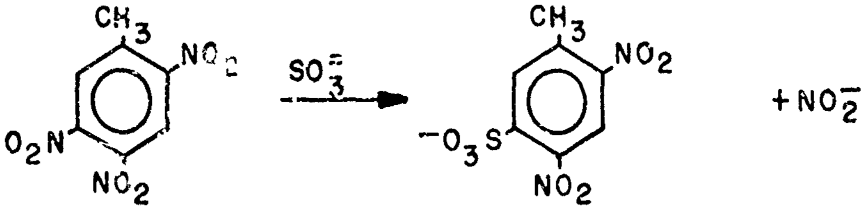
and the reaction is reversible with acid according to D. G. Gehring[47]. Gehring states that displacement of a nitro group can eventually occur. The principal reaction products (43) from sodium sulfite and unsymmetrical TNT isomers (42) are already characterized;



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however, the 14 theoretically possible isomers from the 5 parent TNT isomers (2, 4, 6-trinitrotoluene not included) should all be pale yellow or colorless. They are very water soluble and should not contribute to the red color of the effluent water from manufacturing of TNT. According to Gehring[47] and the Edgewood Arsenal group[33] there is red coloration after 2 or 3 minutes from the 2, 4, 6-, 2, 3, 4-, 2, 4

5-, and 2, 3, 6-TNT isomers and sodium sulfite solution (initial yellow solution), but this is not attributed to the soluble sulfonate salts of TNT. Rosenblatt, Lauterbach and Davis[35] mention the possible elimination of sodium sulfite in the future manufacture of TNT, which would eliminate water pollution from that source. They report that present treatment of sulfite red water has decreased considerably the pollution caused by the Sellite process. Because of information already available in the literature and the fact that no major pollution problem from sulfonate salts exist, sodium sulfite was not considered for laboratory studies.

Literature sources and laboratory studies indicate alkali hydroxides form red compounds with a TNT - water solution very rapidly. Sodium or potassium hydroxide are a good source of base without introducing some other anion such as sulfite or carbonate which would make the characterization of the components formed even more difficult. The alkali hydroxides, therefore become the likely candidates for the red TNT studies. The only reason potassium hydroxide was mainly used was because the perchlorate salt had to be precipitated away from the red TNT at one stage. Potassium perchlorate is less soluble than sodium perchlorate.

A one percent or greater solution of sodium hydroxide readily reacts with TNT. The solution goes from orange to coffee-black as increasing amounts of TNT are added, with stirring, to the alkaline solution. This red TNT concentrate was brought to near pH 7 with hydrochloric acid and flash evaporated. The red TNT - NaCl mass was extracted in a Soxhlet extractor with methanol. The methanol was evaporated and an infrared spectrum of the residue was obtained. As can be seen from figure I, the carbonate bands overwhelm everything else in the spectrum. Even preparing the red TNT in an argon atmosphere did not eliminate carbonate contamination which results from reaction of sodium hydroxide with carbon dioxide in the atmosphere. Because of the carbonate interference with the infrared studies, a more dilute basic solution was considered which was added slowly to TNT - water. Also the more dilute base was consistent with a need for stoichiometric studies of the reaction.

A titration method was considered for trying to learn more about the stoichiometry of the reaction between base and TNT. Titration methods in organic solvents are mentioned in the literature, but TNT and alkali or organic basic materials would not react the same in these media as they would in aqueous media. Urbanski[48] mentions that TNT is an acid 10^{13} times weaker than picric acid. Certainly attempts at titration in aqueous media would be futile in light of the virtually non-existent acidic properties of TNT.

B. Production of Red TNT

When preparing solutions for red TNT production the TNT was added to distilled water and allowed to dissolve. This usually took at least two days of stirring. The solubility of TNT in water at room temperature is only 0.015%. After TNT

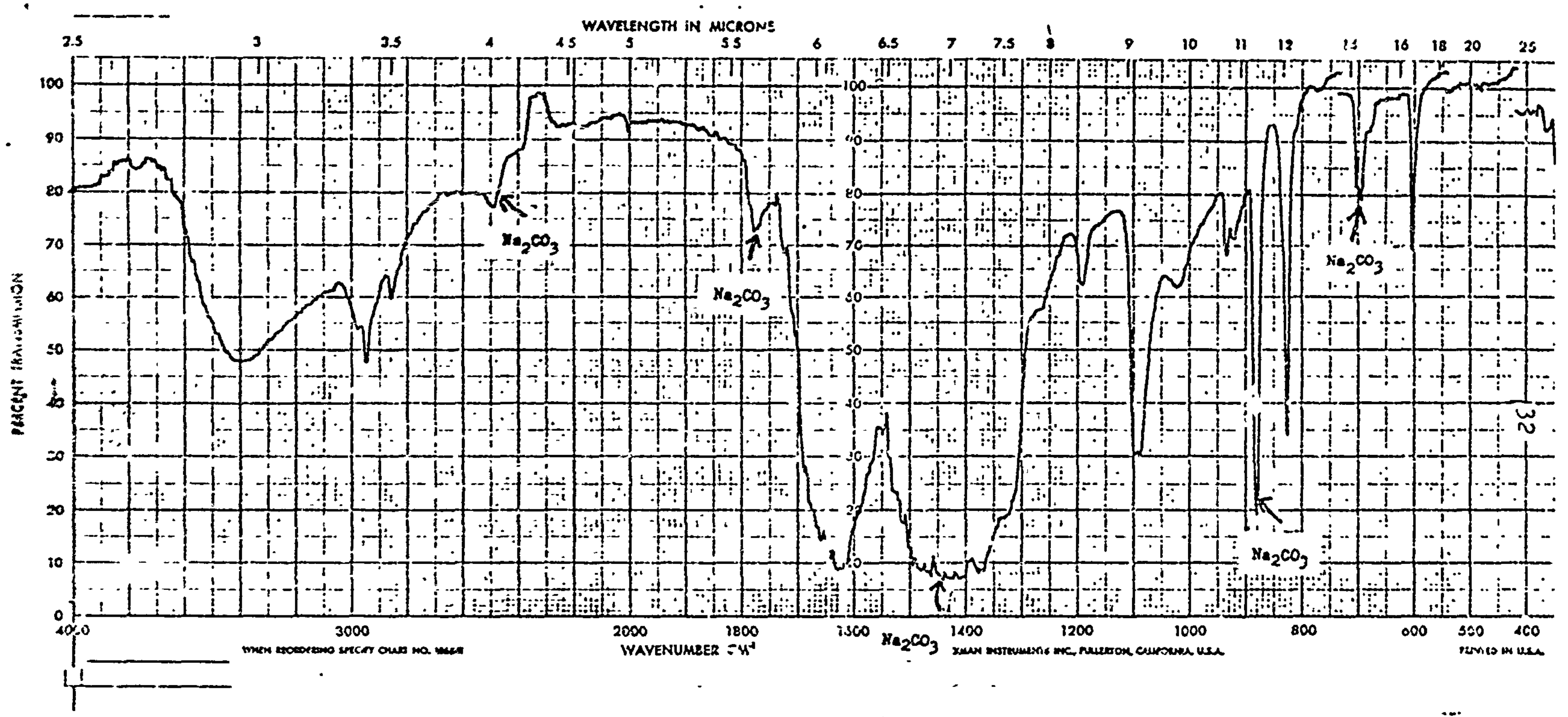
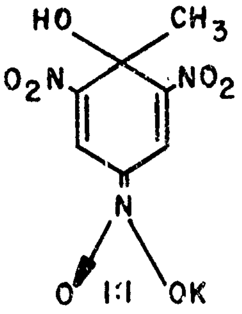


Figure I. Infrared spectrum of red TNT contaminated with sodium carbonate was dissolved in the water, potassium hydroxide solution was added. The use of excess alkali was abandoned because of formation of carbonate. Most of the red TNT obtained was formed from 0.227 gram of TNT dissolved in three liters of water. To this was added 1:1, 2:1 and 3:1 mole ratios of potassium hydroxide to TNT. These molar ratios were used because it was felt that the compounds (44), (45) and (46) could be formed.



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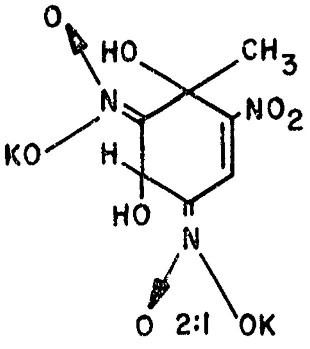

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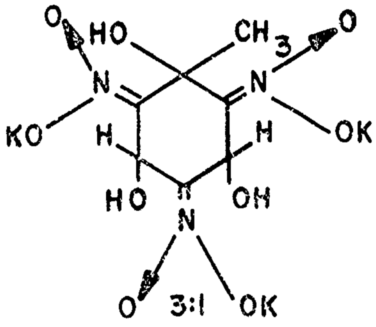

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The three liter solution of TNT and water was stirred while the potassium hydroxide solution (0.1N or less) was added slowly. Addition usually occurred over a period of about one hour. After complete addition of potassium hydroxide the solution initially would be pinkish - red, but on standing (one or more hours) the color would change to red - orange. The solution was either used directly for visible - UV studies or reduced to a small volume by flash evaporation. During flash evaporation insoluble crystals would appear. They were pink and were filtered out periodically during reduction of solution volume. They were examined by infrared spectrophotometry and were identified as TNT, except that an extra prominent methylene band in the carbon-hydrogen stretching region was noted in the case of the 2:1 KOH-TNT product. Figure II shows the methylene bands at 2860 cm^{-1} and 2930 cm^{-1}. These bands are not prominent in the spectrum of TNT, as seen in figure III.

C. Isolation of Red TNT

The isolation of the red products from aqueous solution was performed in a variety of ways. Flash evaporation was used to concentrate the liquor or to isolate the solid. The concentrate was freeze dried to obtain a dry material for infrared analysis or elemental analysis. The concentrate was also used for direct injection onto a liquid chromatographic column. The separated components from the liquid chromatograph were collected and the fractions analyzed by visible-UV, infrared, atomic absorption, and elemental and wet chemical analysis.

Other methods of separation were tried with limited success. An ethanol-ether mixture was added to the red TNT-aqueous solution in an effort to precipitate the red TNT. This was done when excess hydroxide was used for production of red TNT. What little red material crystallized out was contaminated with sodium carbonate. Neutralizing with perchloric acid and filtering out the potassium perchlorate from the cold solution was also tried. Some potassium perchlorate still remained in solution with the red TNT after most of the perchlorate had precipitated.

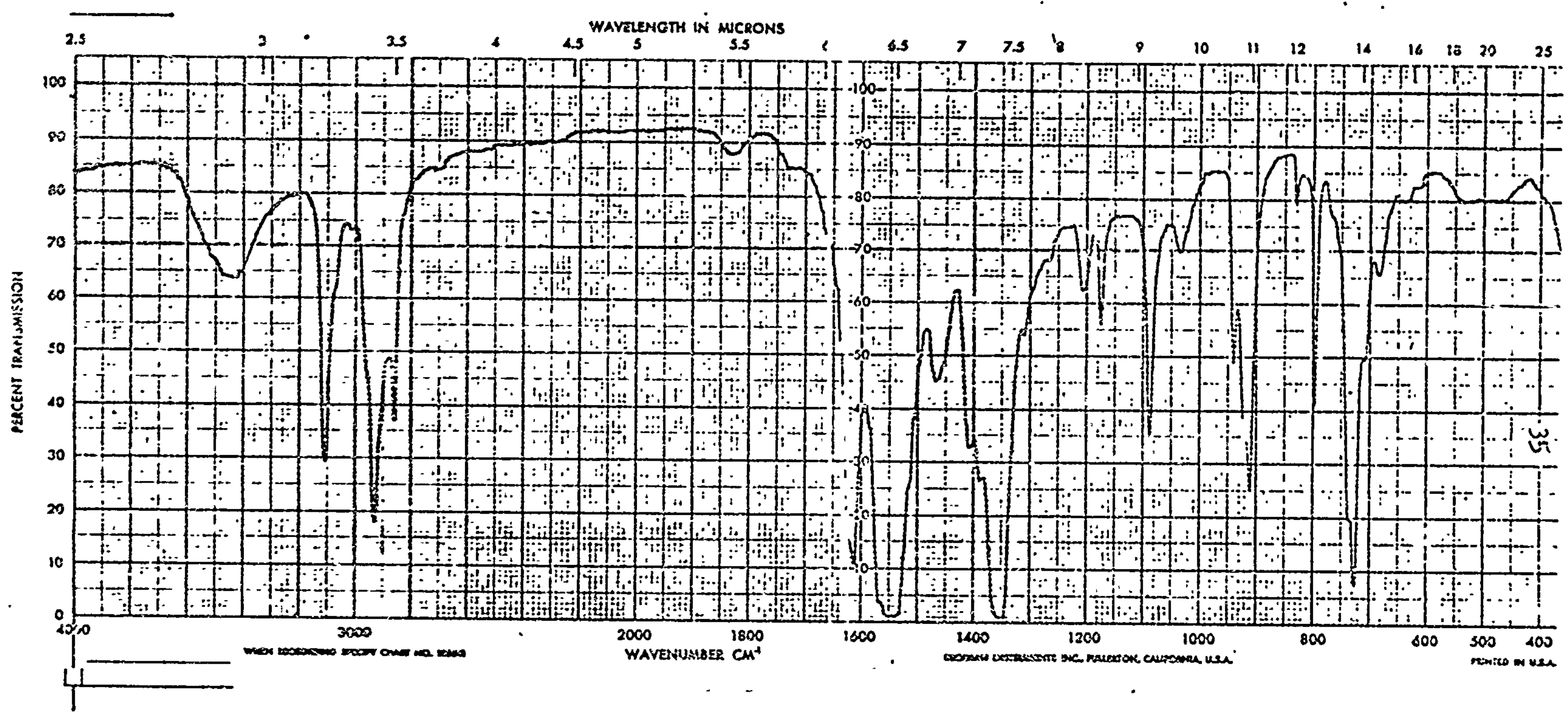


Figure II. Infrared spectrum of pink crystals filtered out during flash evaporation of red TNT.

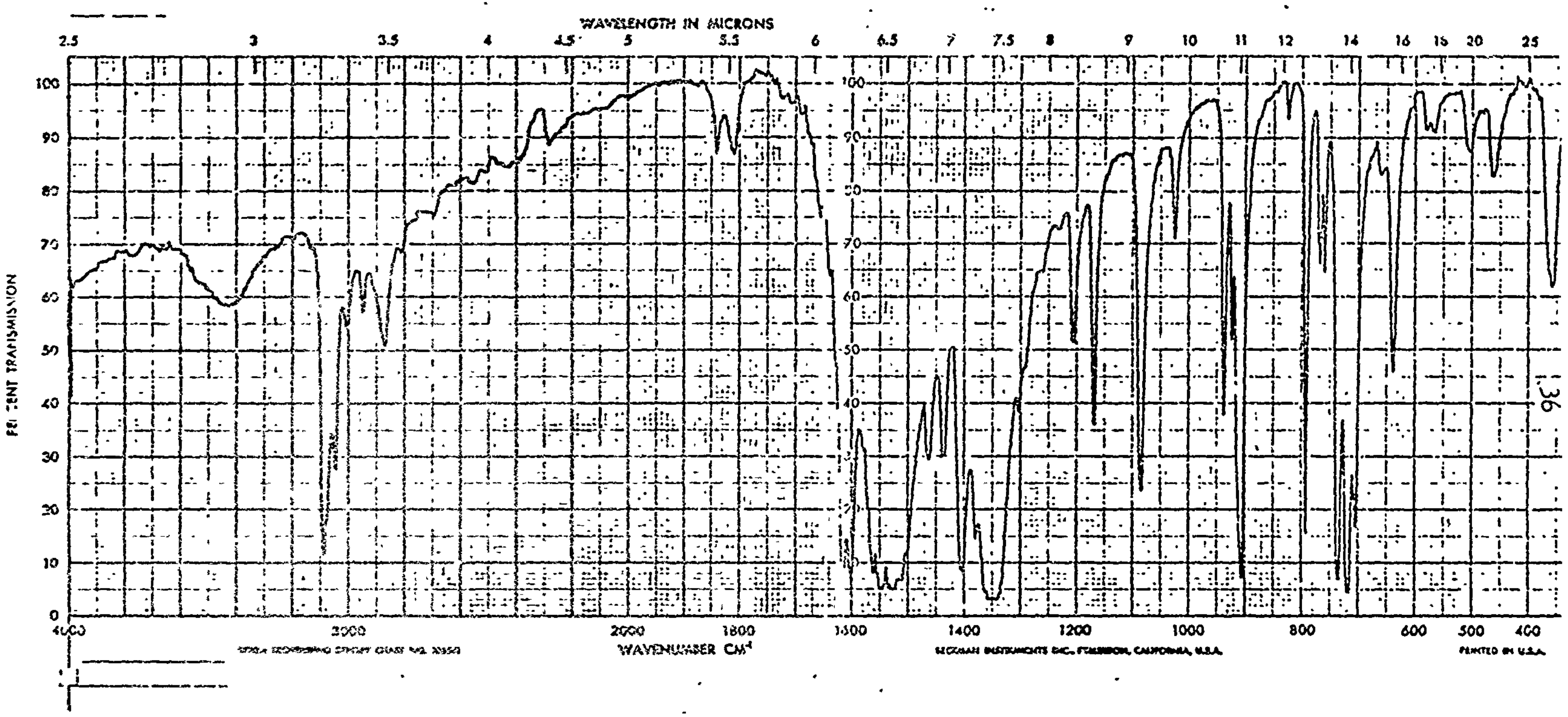


Figure III. Infrared spectrum of recrystallized TNT.

These precipitation techniques could not be used when small concentrations of hydroxide were used. When 1:1, 2:1 and 3:1 mole ratios of KOH to TNT were used it was found that crystallization of TNT occurred during flash evaporation. The evaporation had to be interrupted periodically to filter off the TNT (identification verified by infrared). This left small amounts of red TNT after complete evaporation. Insufficient sample was a problem when using a technique such as elemental analysis.

Some components separated as fractions from the liquid chromatograph were freeze dried. The material, although solid in a vacuum, immediately turned to liquid at atmospheric pressure.

D. Analytical Techniques

A variety of analytical methods were used to study the solutions and the isolated solids from the TNT-alkali reaction. Among these methods were infrared spectrophotometric analysis, visible-UV spectrophotometric analysis, elemental analysis, mass spectrometric analysis, atomic absorption analysis, thin layer chromatographic analysis, liquid chromatographic analysis, and wet chemical analysis. Most of these analytical methods were used together on the same sample.

1. Mass Spectrometric Analysis

Results using mass spectrometric analysis were very disappointing. None of the red TNT materials used were volatile enough to give a detectable beam required for mass spectrometric analysis. When the temperature of the sample was increased the material decomposed, as evidenced by a carbon dioxide peak. If the red TNT components are potassium salts, then this would explain their lack of volatility.

2. Visible - Ultraviolet Spectrophotometric Studies

Scans of TNT and alkali were made in the visible (350 - 600 millimicrons) and ultraviolet (200 - 350 millimicrons) regions of the spectrum. Among the numerous studies conducted were (1) following the reaction in methanol - water solutions, (2) studying the effects of changes in pH, (3) examination of liquid chromatographic fractions, (4) monitoring the growth and decay of absorption bands during reactions and the possible detection of isosbestic points.

It should be noted at the outset that TNT in water has no absorption until the ultraviolet region is reached, whereupon there appears a broad absorption band peaking at around 230 - 235 millimicrons. The UV scan in figure IV shows TNT's characteristic absorption.

A possible isosbestic point was observed when TNT and sodium hydroxide were reacted in methanol - water media. The point is not truly stationary, however, in that all spectral scans do not pass exactly through the same point. A variable isosbestic point very likely means there are competing or sequential equilibria present. The decay of the 510 millimicron band and growth of the 460 millimicron band are not equal in

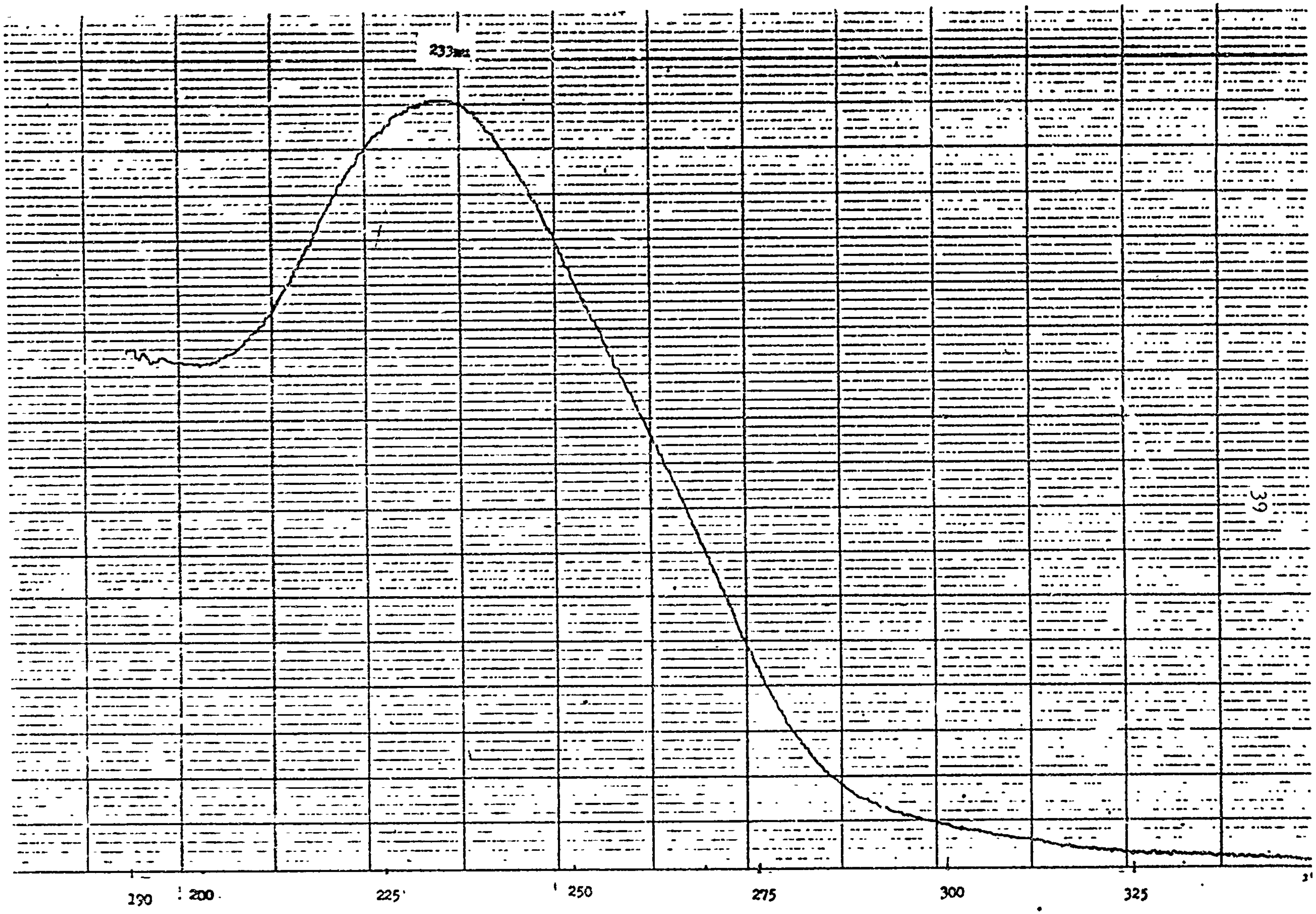


Figure IV. Ultraviolet spectrum of TNT in water rate. This was observed in an 80% methanol - 20% water solution. As can be seen from the scans at various time intervals (figure V), the 510 millimicron band appears to have a hypsochromic shift while diminishing in intensity and finally growing into the 460 millimicron band. Notice the initial appearance of a band at 370 millimicrons. This is more prominent in the scan made in 90% methanol - 10% water, included as figure VI. This absorption band becomes a part of a broad absorption after several hours of reaction time.

These characteristic spectra are in keeping with what Bernasconi[11] reported. The spectrum in basic methanol - water (90 - 10) is very similar to Bernasconi's calculated spectrum of TNT^- in methanol. In an 100% aqueous system there is a strong absorption band at 460 millimicrons with a very slight shoulder visible at 510 millimicrons. The shoulder can be seen on close examination of figure VII. As can be seen from figure VIII during the first ten minutes of the reaction of base with TNT in water, the band at 460 becomes more intense then begins to diminish. The 510 shoulder is not affected until the 460 band has almost given way to the broad intense absorption that starts at about 400 millimicrons and carries into the ultraviolet (at least to 220 millimicrons). Initially formed red TNT has an absorption band at 240 millimicrons too. With time this band is lost in the broad 400 - 220 millimicron absorption envelope. The illustrated scans of 10 ppm (figure IX) and 50 ppm (figure VII) TNT in water show the 510 millimicron band and its persistence for some time during the reaction of TNT with

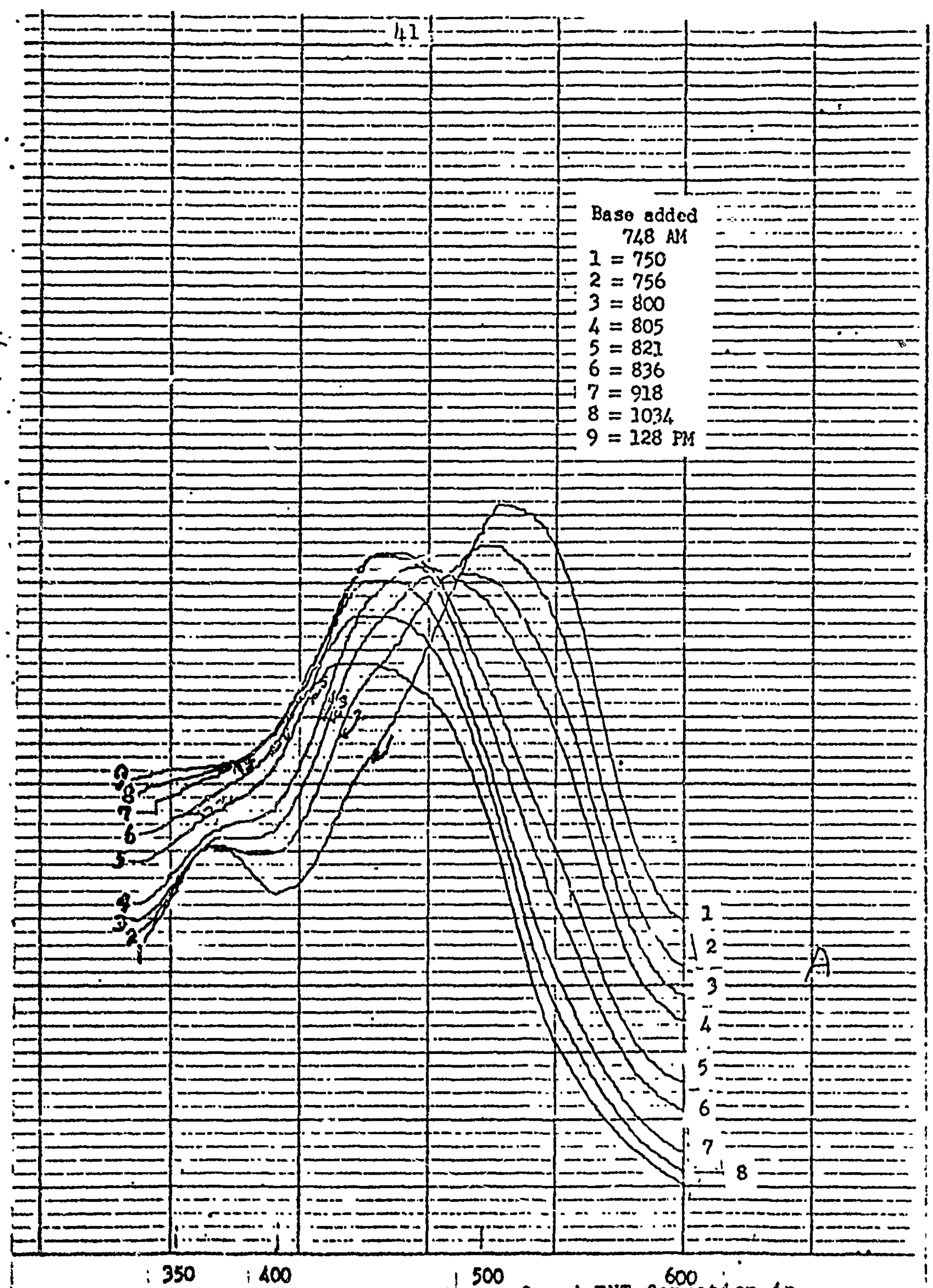


Figure V. UV-Visible spectrum of red TNT formation in 80-20 methanol-water

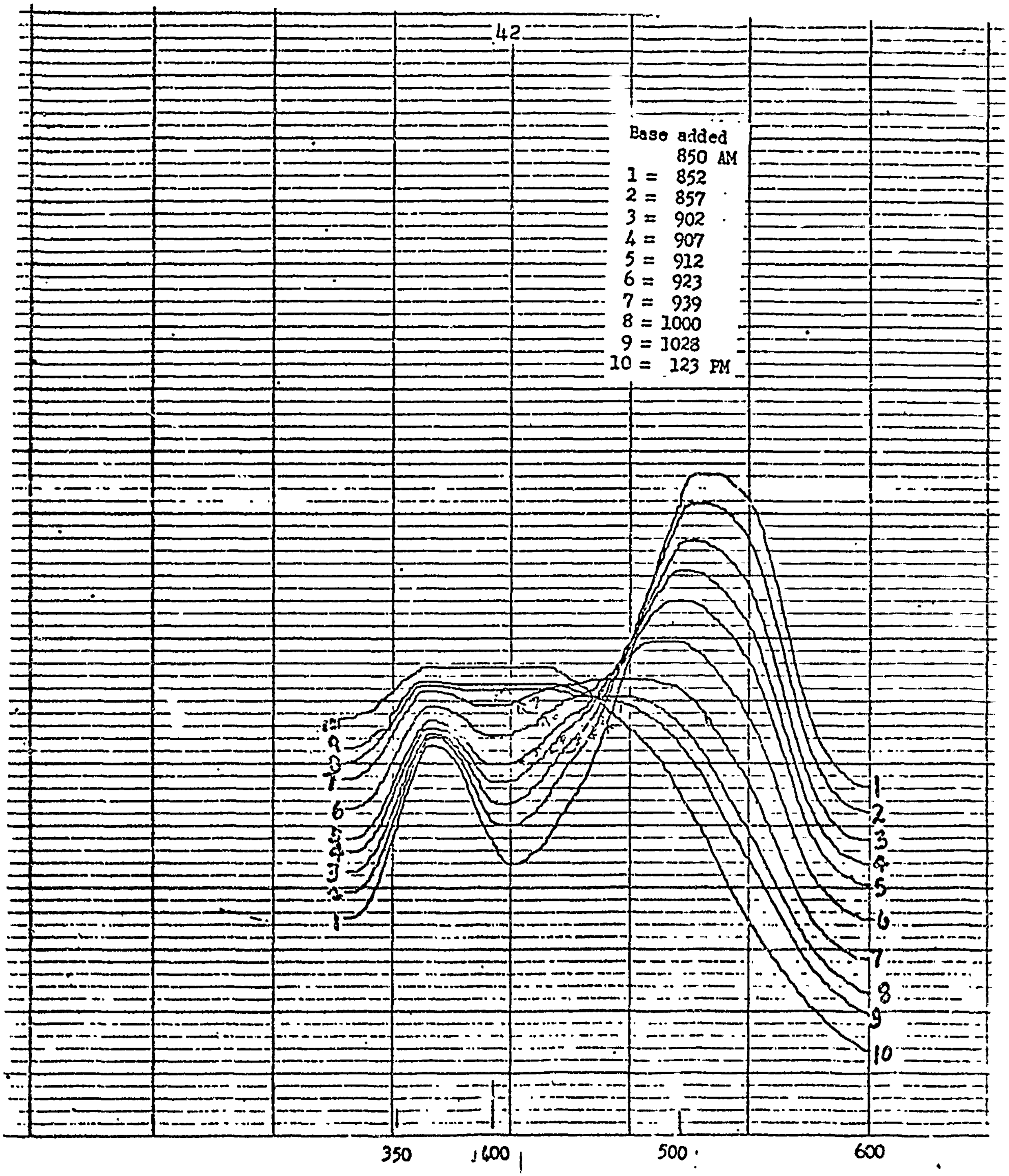


Figure VI. UV-Visible spectrum of red TNT formation in 90-10 methanol-water

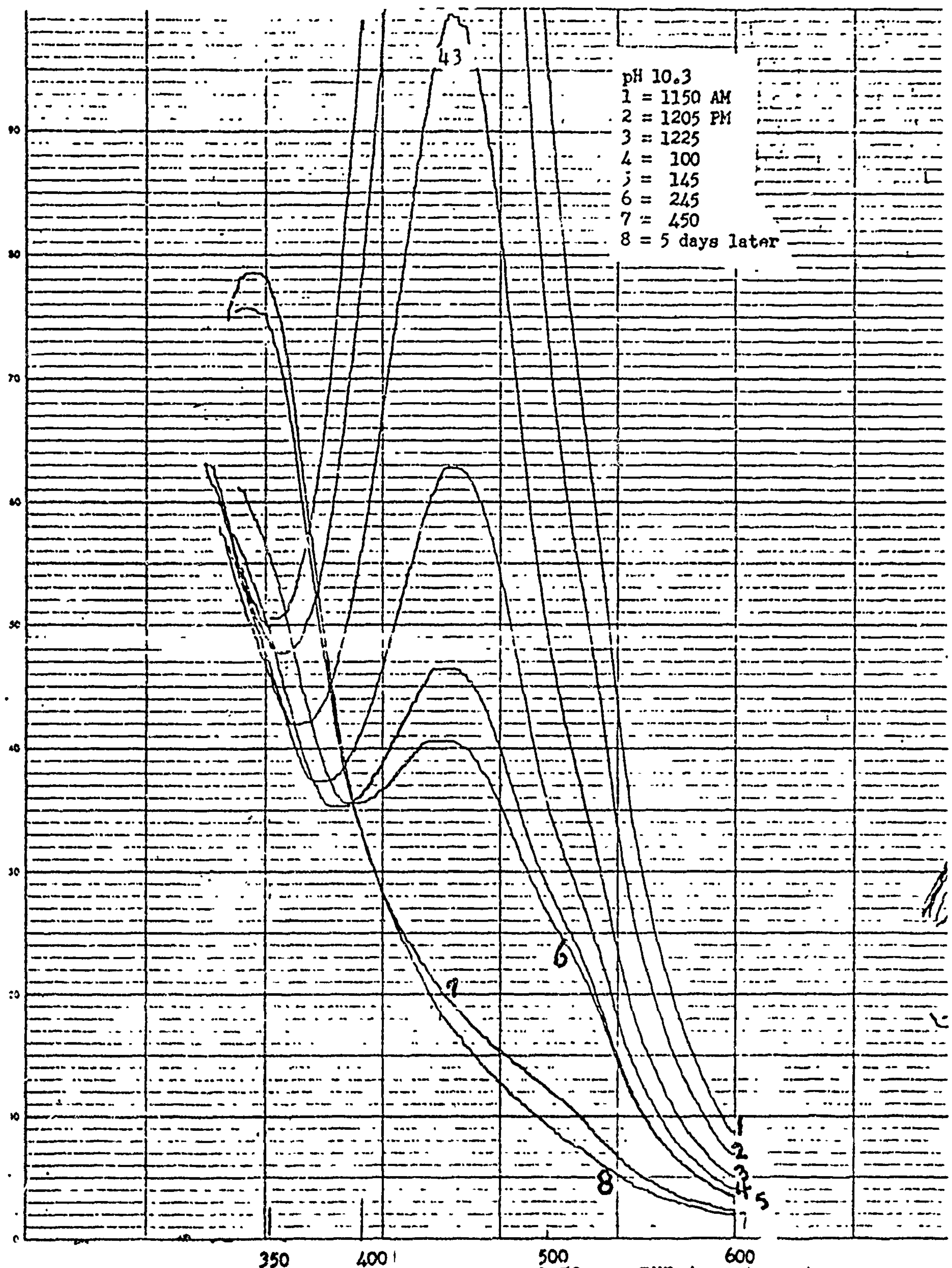


Figure VII. UV-Visible spectrum of 50 ppm TNT in water at pH 10.3.

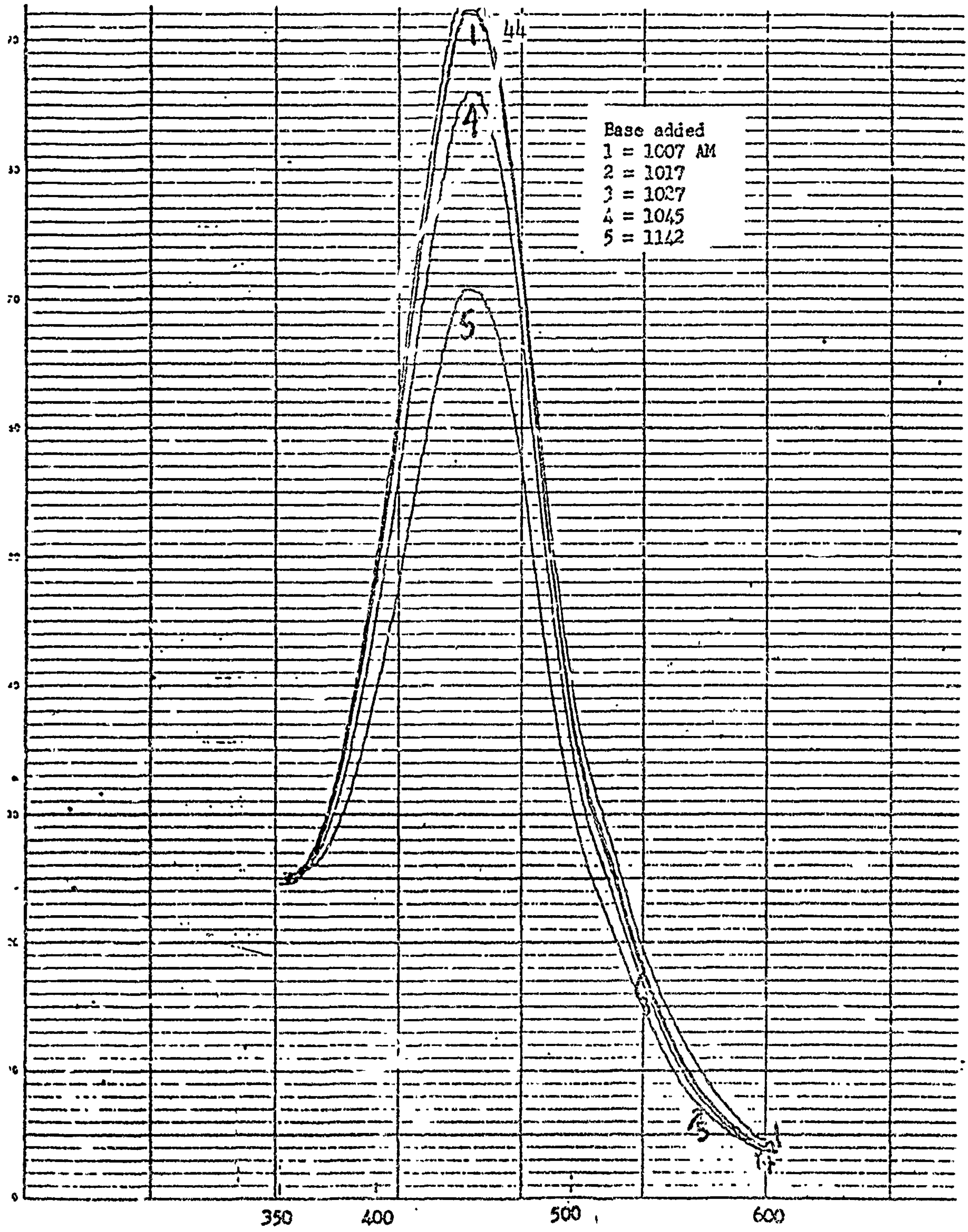


Figure VIII, UV-Visible spectrum of 20 ppm TNT in alkaline solution

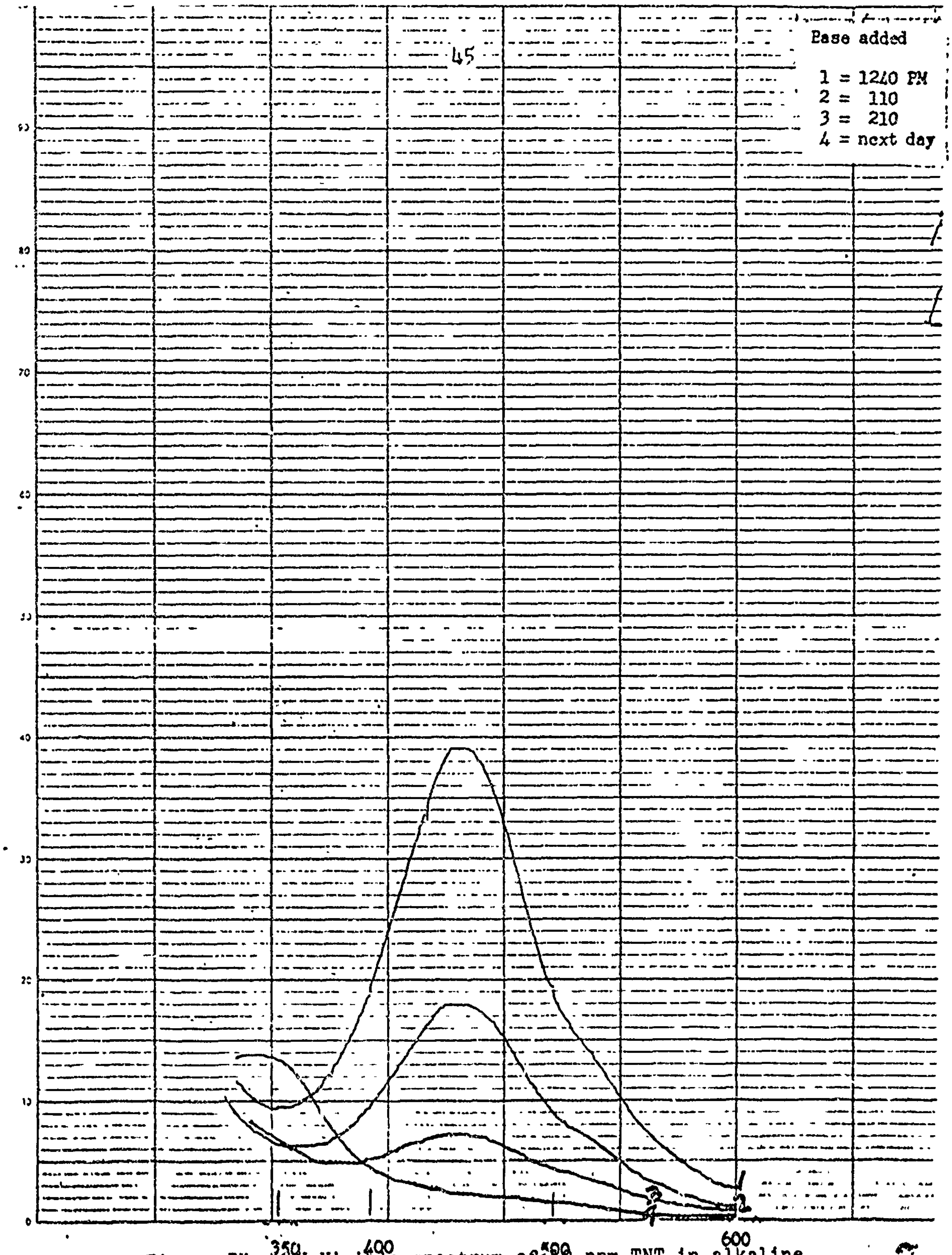


Figure IX. UV-Visible spectrum of 10 ppm TNT in alkaline solution base. If the TNT anion is present in the purely aqueous system its contribution to the visible - UV spectrum is very slight. If the 510 millimicron shoulder is due to TNT^- then it is not too surprising that the 370 millimicron band is not observed because, according to Bernasconi[11], the 370 band is weaker than the 510 band.

Numerous spectra were generated in the ultraviolet region 200 - 350 millimicrons. These spectra were obtained in conjunction with liquid chromatographic studies and will be dealt with later.

E. Separation Techniques

Various methods were used to examine red TNT to see if it was composed of more than one component. The separation methods tried were thin layer chromatography, ion exchange resins and liquid chromatography. The latter method proved the most successful. Atomic absorption analysis, elemental analysis, and wet chemical tests were used in conjunction with liquid chromatography. Infrared spectrophotometric analysis was used with all the separation techniques employed.

1. Thin Layer Chromatography

One dimensional development on Silica Gel G plates was employed for thin layer studies. After development the components which moved from the starting point were colorless and had to be detected by an ultraviolet light. The component which did not move was light brown in color. The separated components were scraped from the plate, dissolved in methanol, and the Wick-Stik technique was used to get a sample for infrared spectrophotometric analysis. The following developing solvent mixtures eluted one component which traveled with the solvent front, one component which was intermediate and one component which remained stationary:

Methanol-Acetic Acid-Water: 83-5-12

Methanol-Water: 95-5

Dioxane-Methanol: 90-10

Later experiments with methanol were conducted using Silica Gel plates that could be cut into pieces so that the component could be dissolved from the pieces and concentrated by the Wick-Stik method. A yellow component was obtained for analysis. This component was near the solvent front and was barely separated from the red component at the solvent front. The only information obtained from the infrared spectra was possible symmetric and asymmetric stretching bands for the nitro group. The C=N band of a nitrorate salt could be included in the Asymmetric nitro band at 1570 CM^{-1}. These bands are the strongest in the spectrum as can be seen from figure X.

2. Ion Exchange Resin Studies

A Dowex 50W-X8 cation exchange resin did not retain any colored component from a red TNT solution. Two basic anion exchange resins were used. They were Rexyn AG1 ($Cl-SO_4$ form) and Dowex 21K. Both produced similar results. They retained one colored component and allowed another colored component to

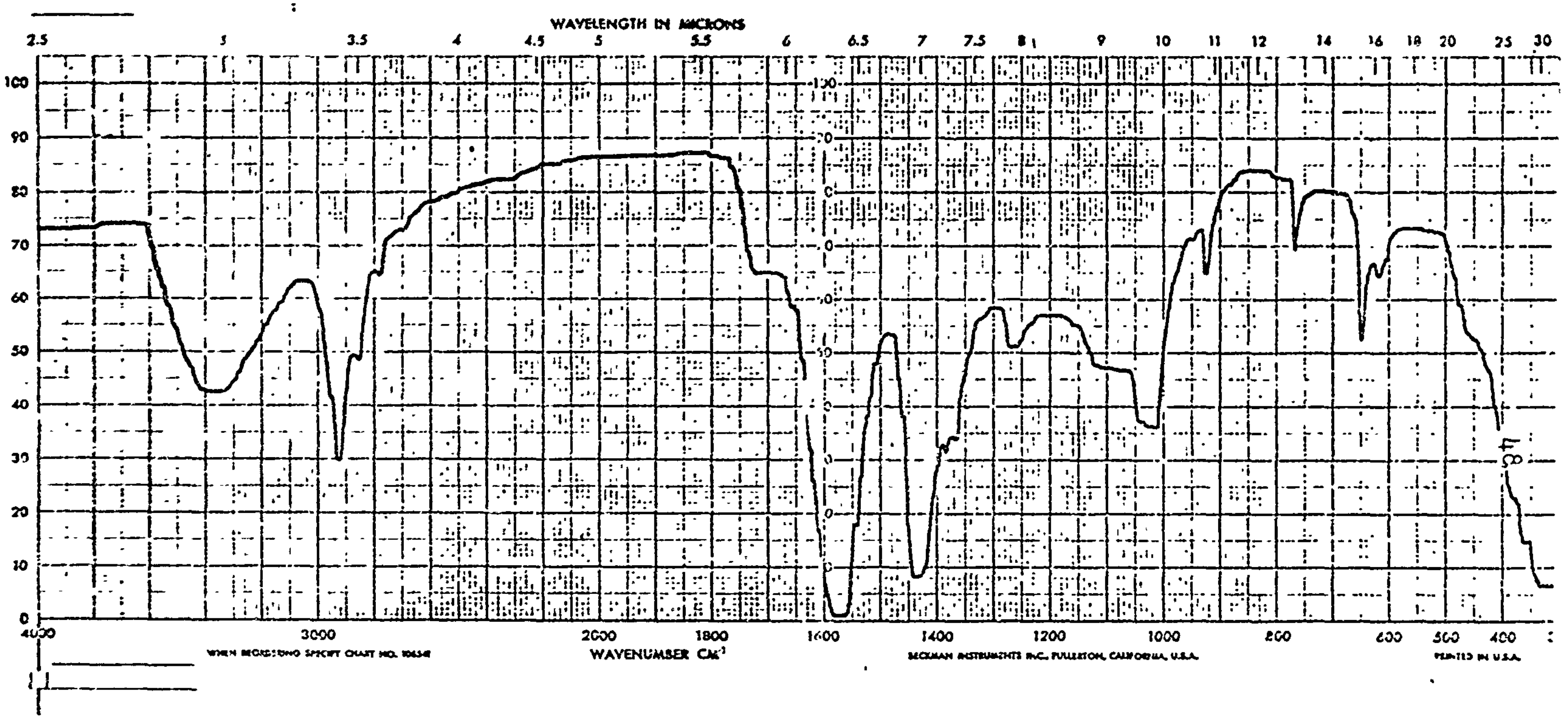


Figure X. Infrared spectrum of yellow material from thin layer chromatographic plate pass through. Infrared spectrophotometric analysis of the emerged components was obtained but no interpretation could be made.

3. Liquid Chromatography and supporting analytical techniques

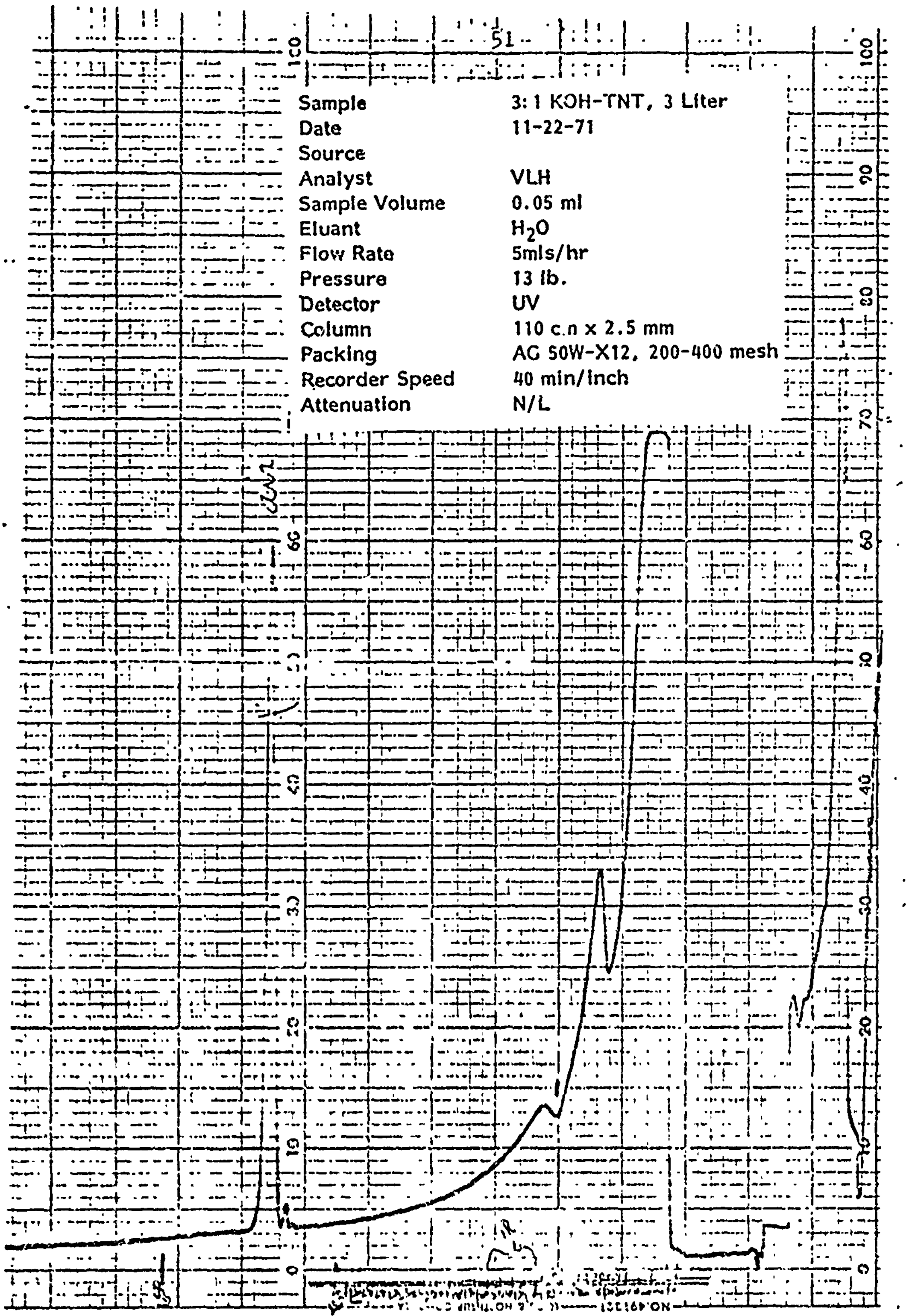
Liquid chromatographic analysis was the most effective method for separating and isolating components contained in red TNT. The separated fractions were studied by infrared spectrophotometric analysis, visible-ultraviolet spectrophotometric analysis, atomic absorption spectrophotometric analysis, elemental analysis (carbon, hydrogen and nitrogen) and wet chemical tests.

The liquid chromatograph was fabricated from commercially available pumps, UV detectors, RI detector, fraction collector, and various column and plumbing hardware. A chemist in the Sciences Branch at U. S. Naval Ammunition Depot, in Crane, Indiana, assembled and designed the chromatograph for water pollution studies. The first sample of a pollution nature run on the system was TNT-water solution. A very symmetrical peak for TNT was obtained. The UV monitor operates at a wavelength of 254 millimicrons. There were two separate pumps used throughout the studies. Pumping speeds from 1 ml/hr to 120 mls/hr were available. The fraction collector was capable of automatic operation and an event marker was used to indicate where fractions were collected in reference to the chromatographic peaks. The length of time of each fraction could also be set. Various column dimensions and a variety of packing materials were investigated. The packings used were Sephadex G-10, Sepharose 4B, Sepharose 6B and AG 50W-X12.

The liquid chromatograph was equipped with sample injector loops. The sample volume was changed merely by changing the size of the sample loop. The tubing was transparent enough to allow visual monitoring of the red colored sample and its location. The columns were made out of glass and the column packings were either white or almost colorless. This allowed visual observation of the red TNT as it proceeded down the column. A flow monitor allowed accurate measurement of the flow rate. When the flow was 120 mls/hr, as designated by the pump setting, the actual flow rate was usually around 105 mls/hr since the remaining 15 mls/hr was to the reference side of the detector. All these facts are alluded to in the detailed description of the liquid chromatographic studies that will follow.

a. AG 50W-X12

A column 110 centimeters long and 2.5 millimeters inside diameter was packed with the resin AG 50W-X12. A sample of concentrated red TNT solution from a 3 liter preparation of 3:1 KOH-TNT was injected into the liquid chromatograph. The resulting chromatogram, figure XI, showed three peaks, but they were not resolved sufficiently to do studies on the separate components. Figure XII is an infrared spectrum of the trailing edge of the last peak. It shows only carbon-hydrogen stretching and a possible band at 1380 cm^{-1} due to nitrate. Further work



Sample	3:1 KOH-TNT, 3 Liter
Date	11-22-71
Source	
Analyst	VLH
Sample Volume	0.05 ml
Eluant	H_2O
Flow Rate	5mls/hr
Pressure	13 lb.
Detector	UV
Column	110 cm x 2.5 mm
Packing	AG 50W-X12, 200-400 mesh
Recorder Speed	40 min/inch
Attenuation	N/L

Figure XI. Liquid chromatogram of concentrate from 3:1 KOH-TNT reaction

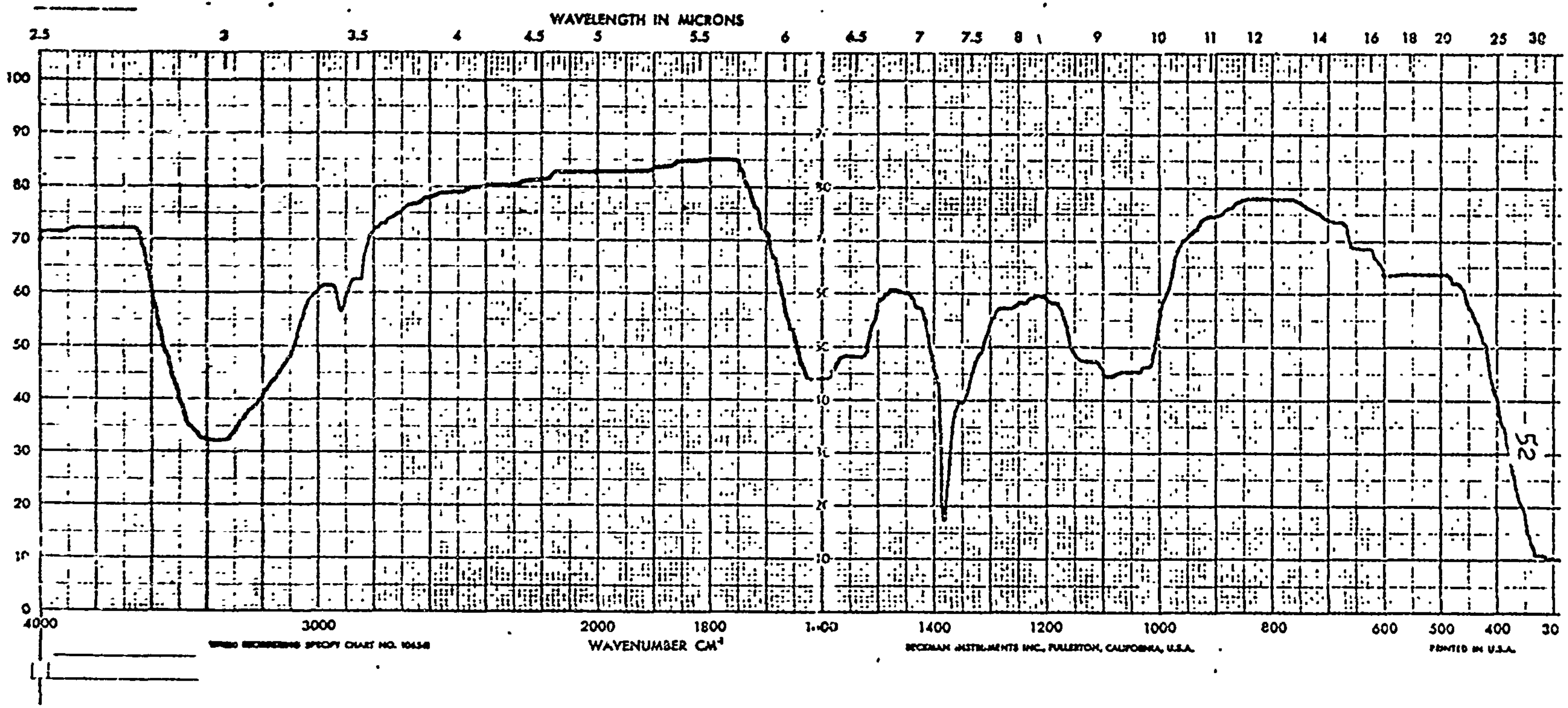


Figure XII. Infrared spectrum of fractions collected from AG50W-X12 liquid chromatographic column with this column material was abandoned because of the poorly resolved peaks.

b. Sephadex G-10

Sephadex is a bead-formed, dextran gel. The molecule is composed of polysaccharide chains containing many hydroxyl groups. Sephadex swells in water and is a chromatographic material capable of separating substances according to their molecular size. The separation method is generally called gel filtration or gel chromatography. Molecules that are larger than the pores of the swollen Sephadex beads will pass through the column rapidly because of inability to penetrate the gel particles. The smaller molecules, however, will spend some time inside the gel particles before they pass on through the column. Large molecular compounds therefore, emerge first and smaller molecular compounds emerge later. The molecular weight exclusion limit as given by Pharamacia Fine Chemicals is 700 for Sephadex G-10. Mulder and Buytenhuys[49] give a word of caution about using stated exclusion limits. Their experience is that the limits are usually too high, and they cite as an example a gel of 5000 exclusion limit being used to effectively separate substances of molecular weight 200 and lower. This could explain the effectiveness of Sephadex G-10 in separating red TNT components.

Maegerlein[50] performed experiments that showed that similar nitro substituted aromatic compounds do not elute in order of their molecular weight when using Sephadex G-10 column packing.

Mulder and Buytenhuys[49] say that aromatics absorb on polydextran gels. Goodson, Distefano and Smith[51], reported on other materials that undergo gel interaction. They mention changes in elution due to hydration.

It can be seen from literature references [49, 51] and experimental evidence[50] that Sephadex does not lend itself as an effective tool for molecular weight determinations of nitro substituted aromatic compounds or compounds capable of hydration. Red TNT components that contain nitro groups, aromatic ring, or hydroxyl groups on the ring may undergo strong interaction with the hydroxyl groups on the polysaccharide chains of Sephadex. Possible hydrogen bonding could occur between the oxygen of the nitro group and hydrogen of the hydroxyl groups in Sephadex.

During the use of Sephadex G-10 it was observed that the initial components of red TNT elute as fast as Blue Dextran (average molecular weight 2000). As previously pointed out this does not mean the initial component could have a molecular weight of 700 or above. Also, some component or components were permanently absorbed by the Sephadex beads. This was visually evident by a red color at the top of the column. The component was apparently small enough to enter the gel bead and had constituents which interacted very strongly with the polysaccharide hydroxyl groups, thus not permitting it to leave the gel bead.

The Sephadex G-10 column consisted of three columns connected in series. Each column was identical, measuring 110 centimeters in length and 2.5 milimeters inside diameter. A sample size greater than 0.5 ml overloaded the column. Flow rates below 16 mls/hr were useless in giving separations. At the low flow rates the peaks were very broad and ran together. Most of the experiments were performed at 105 mls/hr using 0.5 ml sample size. A few runs were made at 16 mls/hr. A refractive index detector was used concurrently with the UV detector on many of the runs. The UV detector gave the most useful information of the two detectors. The fraction collector was used to collect sufficient quantities of each component for infrared and UV-visible studies. Values obtained by infrared and UV instrumentation are tabulated according to main absorption bands in Table I and will be commented on later.

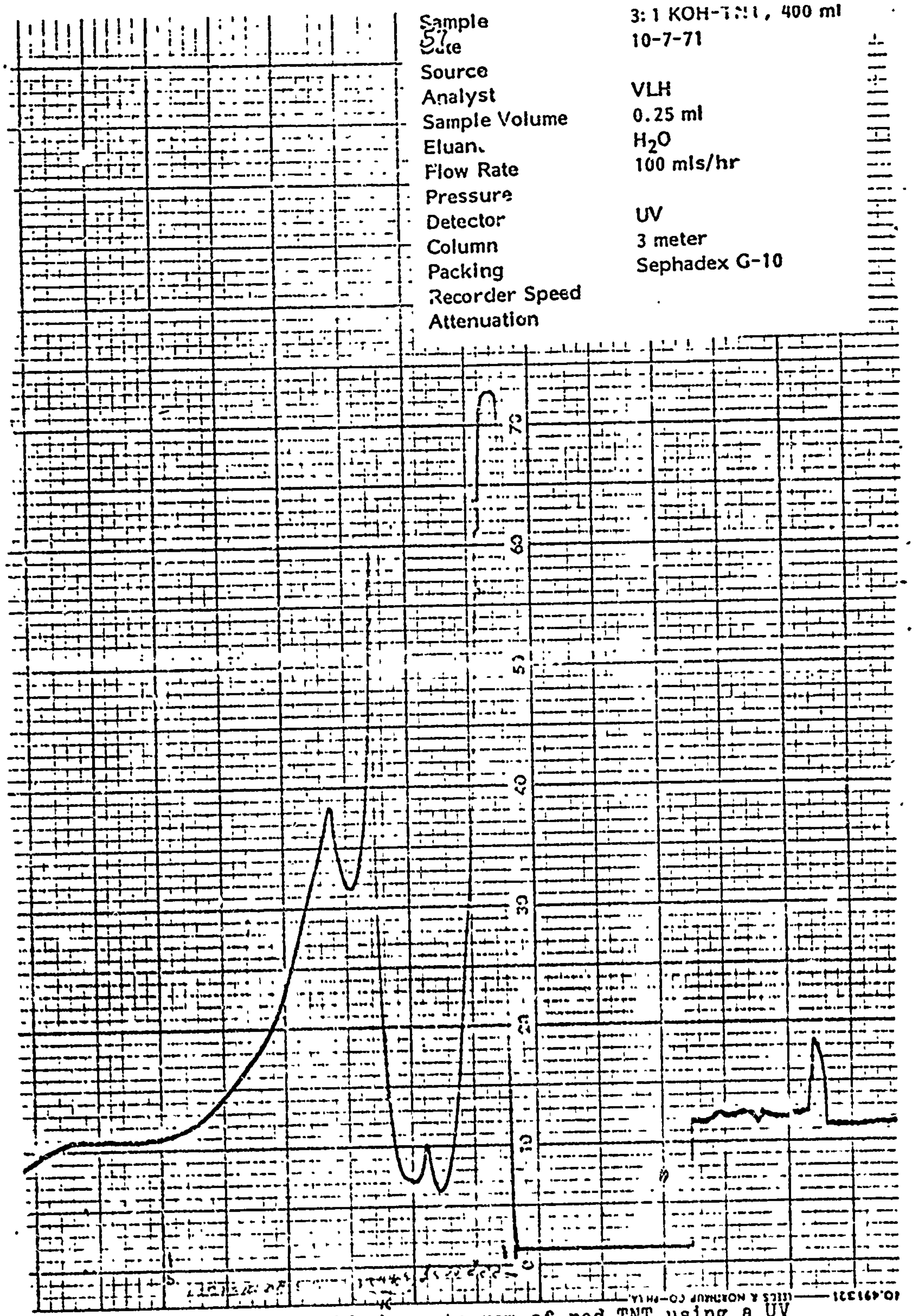
Liquid chromatographic runs of red TNT did not always give reproducible results. The first peak to emerge always occurred at the same retention time but the following peaks were apt to change size, shape, and position. The presence of potassium in the collected fractions was monitored using atomic absorption spectrophotometry for the run shown in figure XIII. The peak for potassium did not always correspond to a peak in the UV detector's chromatogram as will be seen later. The potassium peak did coincide with a peak observed with the refractive index detector. This peak always had a leading edge effect to it. The second largest peak in figure XIV shows this effect. This was because the potassium salt had a greater affinity for itself than for the column packing. At first the Sephadex adsorbs a small quantity of the component; then the quantity already adsorbed attracts more to itself. This tends to arise

Table I

Absorption bands of various samples in ultraviolet and infrared spectral regions

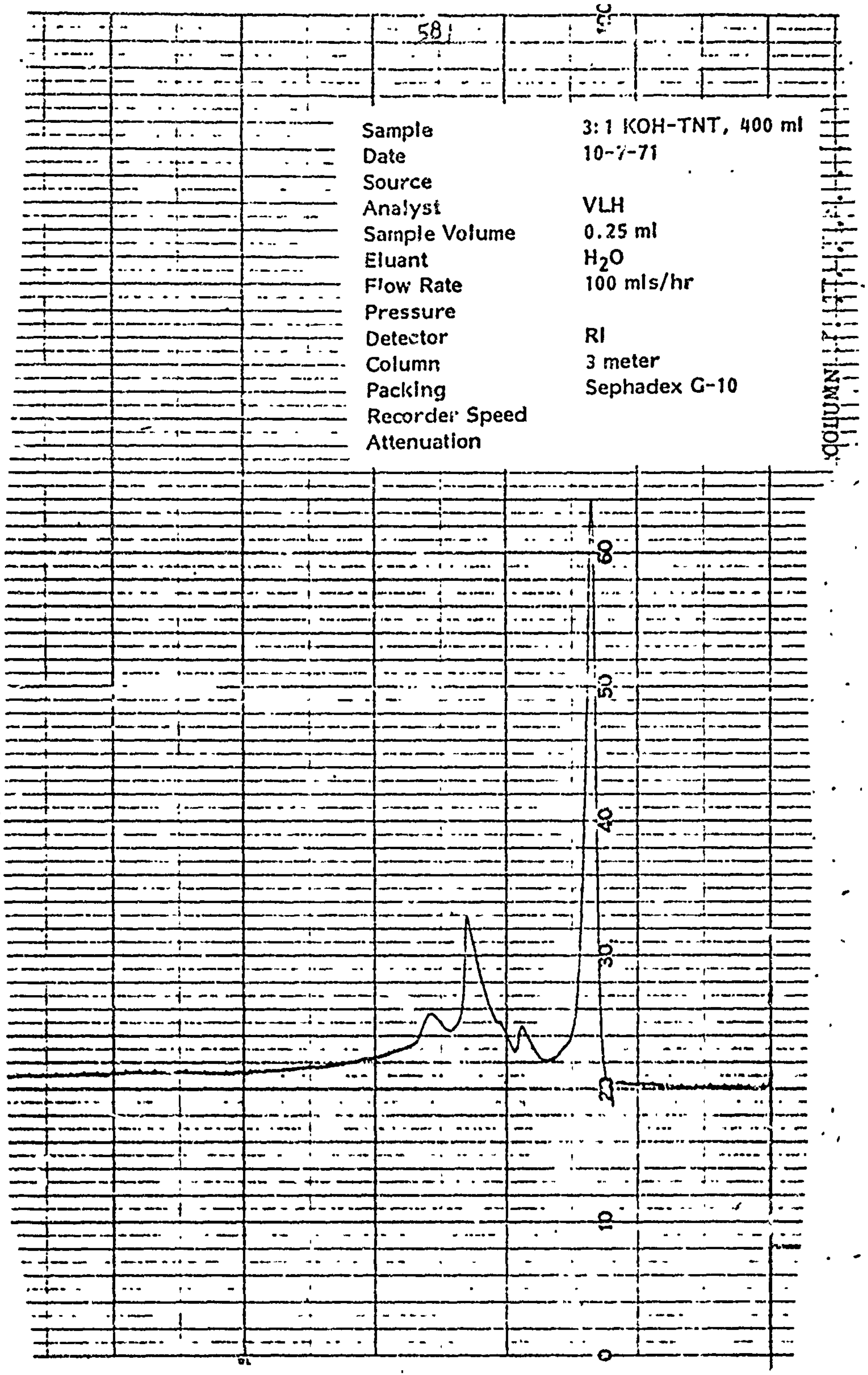
Sample Identification	Date LC^a	UV Peak mu	Infrared Peaks cm^{-1}					
1:1 KOH-TNT, Peak 3, LC	5-25-71	210	3420B^b	2910	2840	1380S^c		
Peak 2, LC	5-25-71	210S						
Peak 4, LC	5-25-71	248						
Peak 3SH^d, LC	5-25-71	225-240B						
Red TNT, Peak 2, LC	11-30-71	209						
Peak 4, LC	11-30-71	208						
3:1 KOH-TNT, 3 Liter, Peak 1,LC	12-2-71		3390B	2910S	2840S	1460	1380S	1000-1100B
Peak 2,LC	12-2-71		3400B	2910S	2840S	1380S	1270	1000-1100B
Peak 3,LC	12-2-71		3390B	2910S	2840	1380S	1270	1000-1100B
Peak 4,LC	12-2-71		3300-3400B		1600B	1380S		1000-1100B
3:1 KOH-TNT, 400ml, Peak 1,LC	10-7-71		3400B	2910	1380B	1020B		
TNT in water		233						
1:1 KOH-TNT flash evaporate	5-25-71		3400B	3100	1600	1540	1350	1250
			1120	905	810	790	720	

^{a}Liquid chromatogram
^{b}Broad absorption band
^{c}Sharp absorption band
^{d}Shoulder



Sample	3:1 KOH-TNT, 400 ml
Date	10-7-71
Source	
Analyst	VLH
Sample Volume	0.25 ml
Eluant	H_2O
Flow Rate	100 mls/hr
Pressure	
Detector	UV
Column	3 meter
Packing	Sephadex G-10
Recorder Speed	
Attenuation	

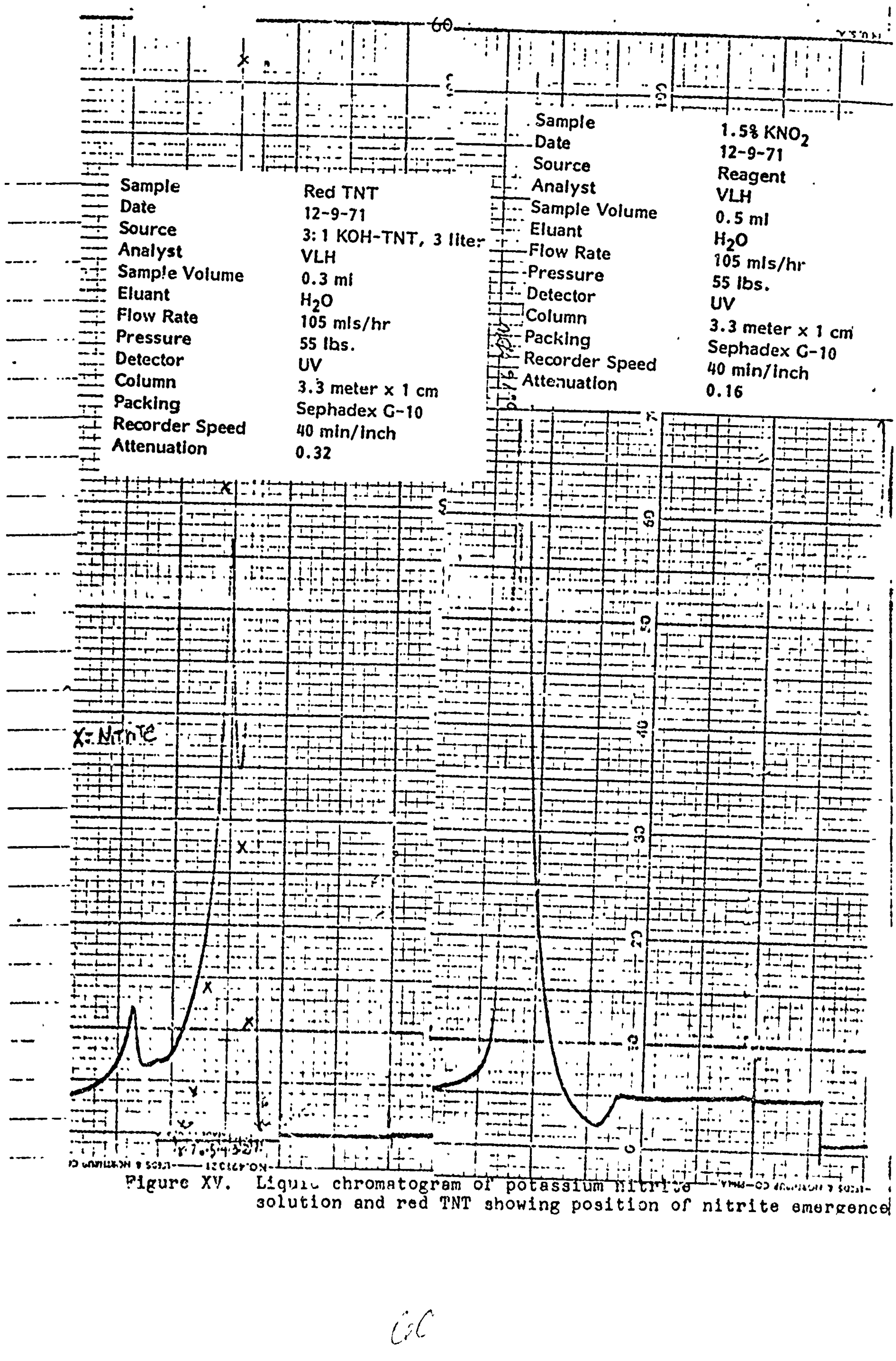
Figure XIII. Liquid chromatogram of red TNT using a UV detector



Sample	3:1 KOH-TNT, 400 ml
Date	10-7-71
Source	
Analyst	VLH
Sample Volume	0.25 ml
Eluant	H_2O
Flow Rate	100 mls/hr
Pressure	
Detector	RI
Column	3 meter
Packing	Sephadex G-10
Recorder Speed	
Attenuation	

Figure XIV. Liquid chromatogram of red TNT using a refractive index detector because of the apparently strong polarity of the potassium salt giving it strong mutual attraction. Nitrite was detected in the fractions by using an absorbing reagent which consisted of sulfanilic acid, acetic acid and N-(1-naphthyl)-ethylenediamine dihydrochloride. The reagent gives a violet color when nitrite is present. Nitrite was detected in the second peak at 60 minutes retention time. Potassium nitrite solution was run under the same column conditions and emerged at 92 minutes as seen from figure XV. Nitrite appearance was not necessarily consistent with potassium appearance. This trend was substantiated in part by results on a 16 mls/hr run. Fractions were collected and tested for both potassium and nitrite ions. The first 62 fractions indicated neither potassium or nitrite ions. Both potassium and nitrite were detected in the 63rd fraction. Both ions were at their maximum in fraction 64. Both decreased in concentration thru fractions 65 to 67. Thereafter no nitrite was detected but potassium remained and tailed off to a small concentration. The UV monitor detected no peak associated with these ions. The refractive index monitor, although operating off scale during part of this time did show changes. These findings are shown in figure XVI. Infrared spectrophotometric runs on fractions from the second and third peaks of a liquid chromatographic run showed a strong absorption band at 1270 cm^{-1} which is characteristic of nitrite. These spectra appear as figures XVII and XVIII.

Red TNT produced from 3:1 KOH-TNT was run on the liquid chromatograph and fractions were collected. The fractions



Sample	Red TNT
Date	12-9-71
Source	3:1 KOH-TNT, 3 liter
Analyst	VLH
Sample Volume	0.3 ml
Eluant	H_2O
Flow Rate	105 mls/hr
Pressure	55 lbs.
Detector	UV
Column	3.3 meter x 1 cm
Packing	Sephadex G-10
Recorder Speed	40 min/inch
Attenuation	0.32

Sample	1.5% KNO_2
Date	12-9-71
Source	Reagent
Analyst	VLH
Sample Volume	0.5 ml
Eluant	H_2O
Flow Rate	105 mls/hr
Pressure	55 lbs.
Detector	UV
Column	3.3 meter x 1 cm
Packing	Sephadex G-10
Recorder Speed	40 min/inch
Attenuation	0.16

Figure XV. Liquid chromatogram of potassium nitrite solution and red TNT showing position of nitrite emergence

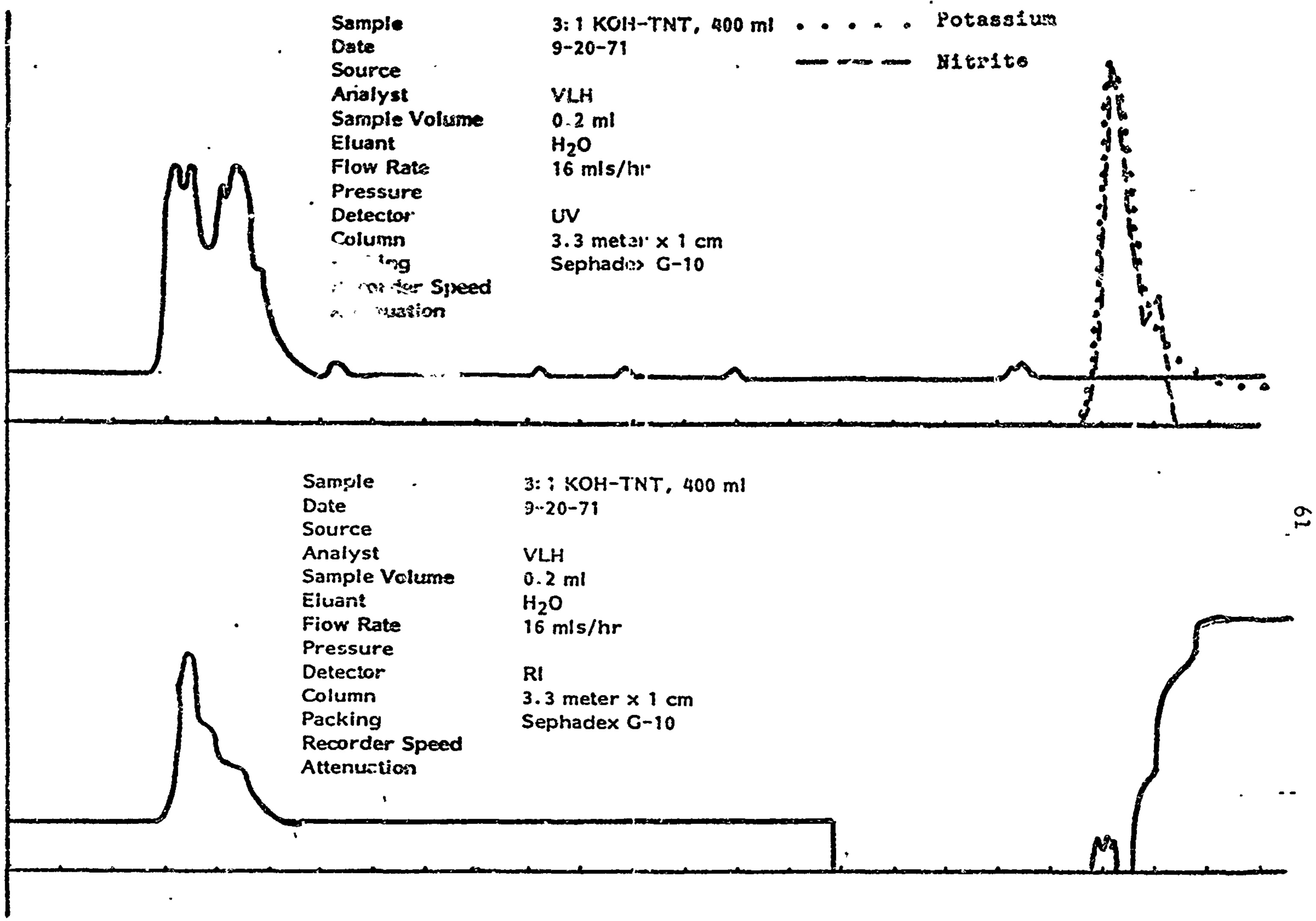


Figure XVI. Liquid chromatogram showing comparison of UV and RI detectors on same run. Potassium and nitrite emergence is shown superimposed on the UV-run.

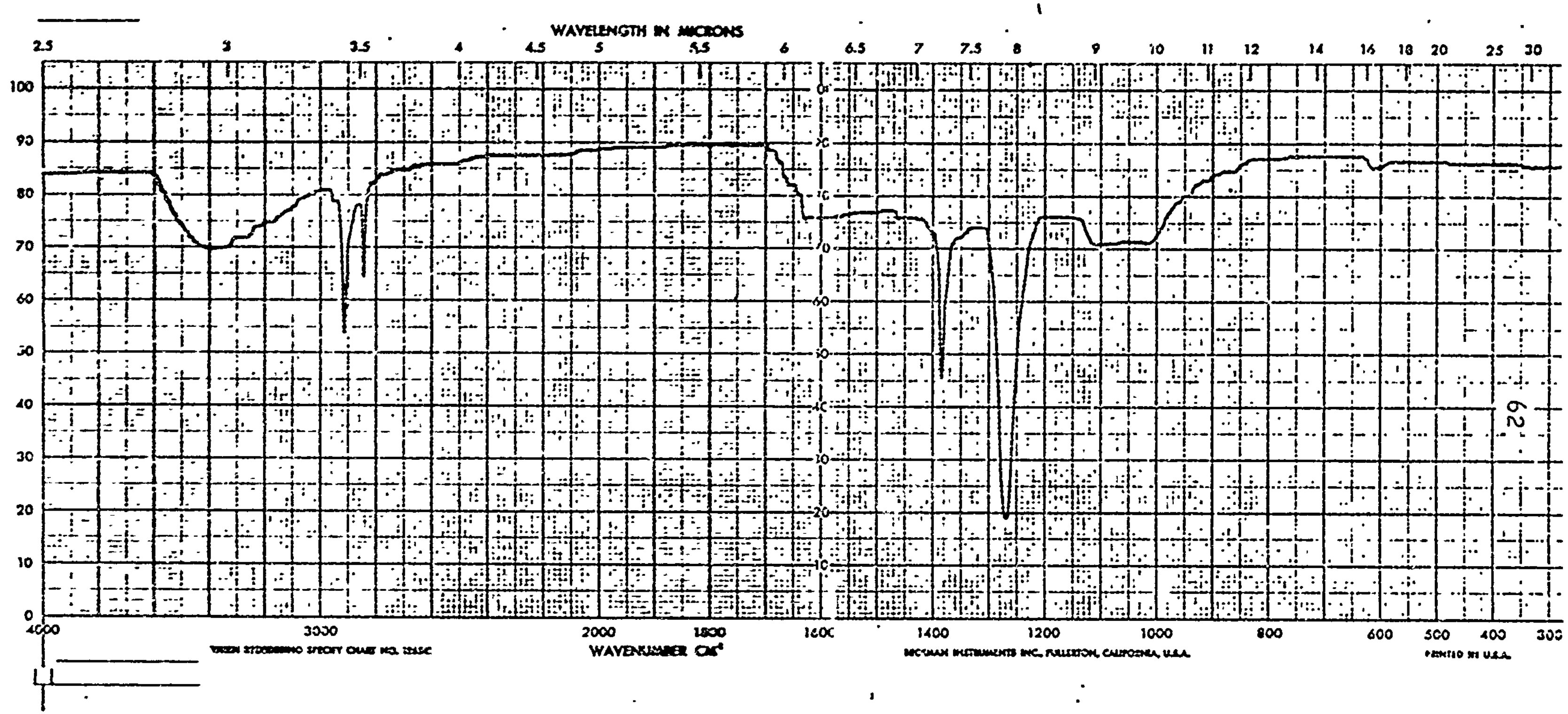


Figure XVII. Infrared spectrum of freeze dried red TNT fraction from second peak to emerge from the liquid chromatograph

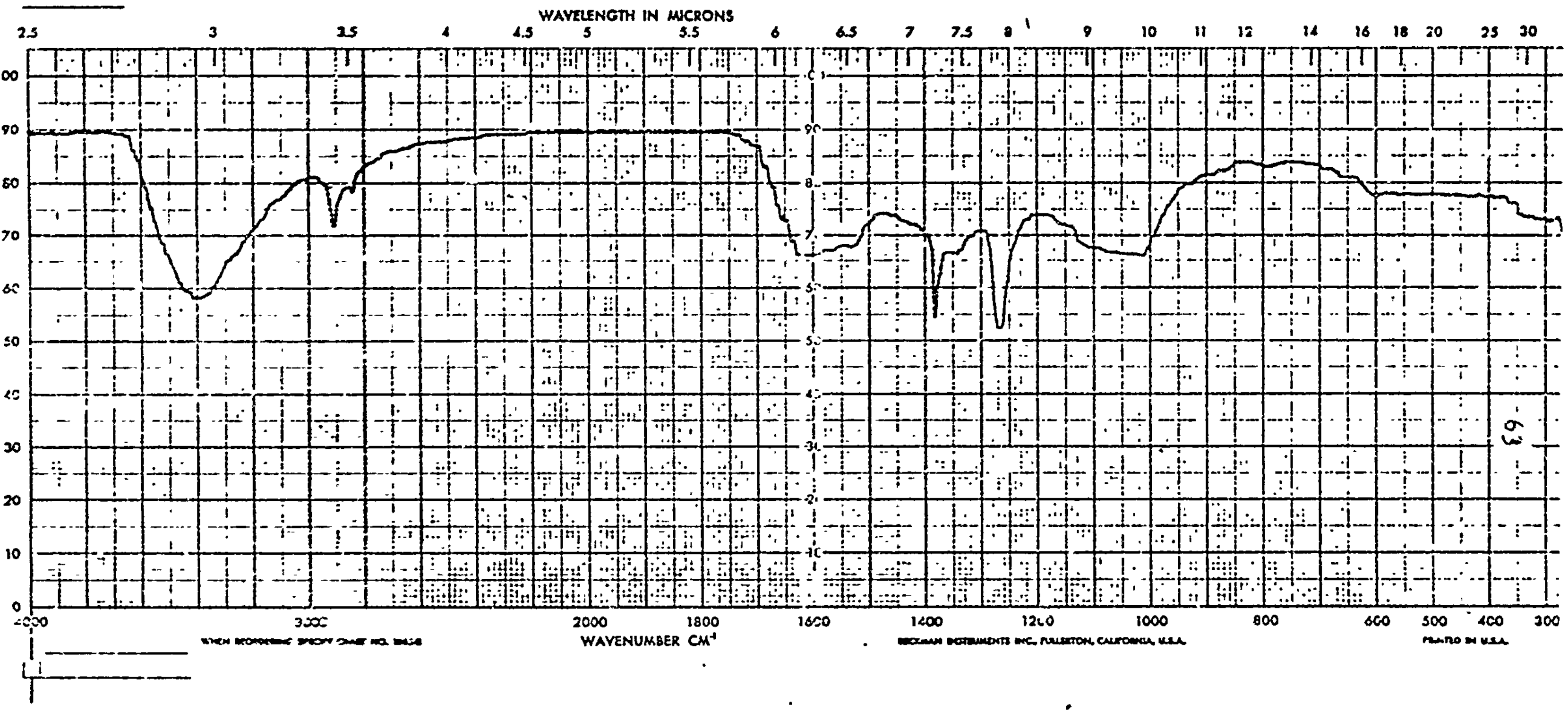


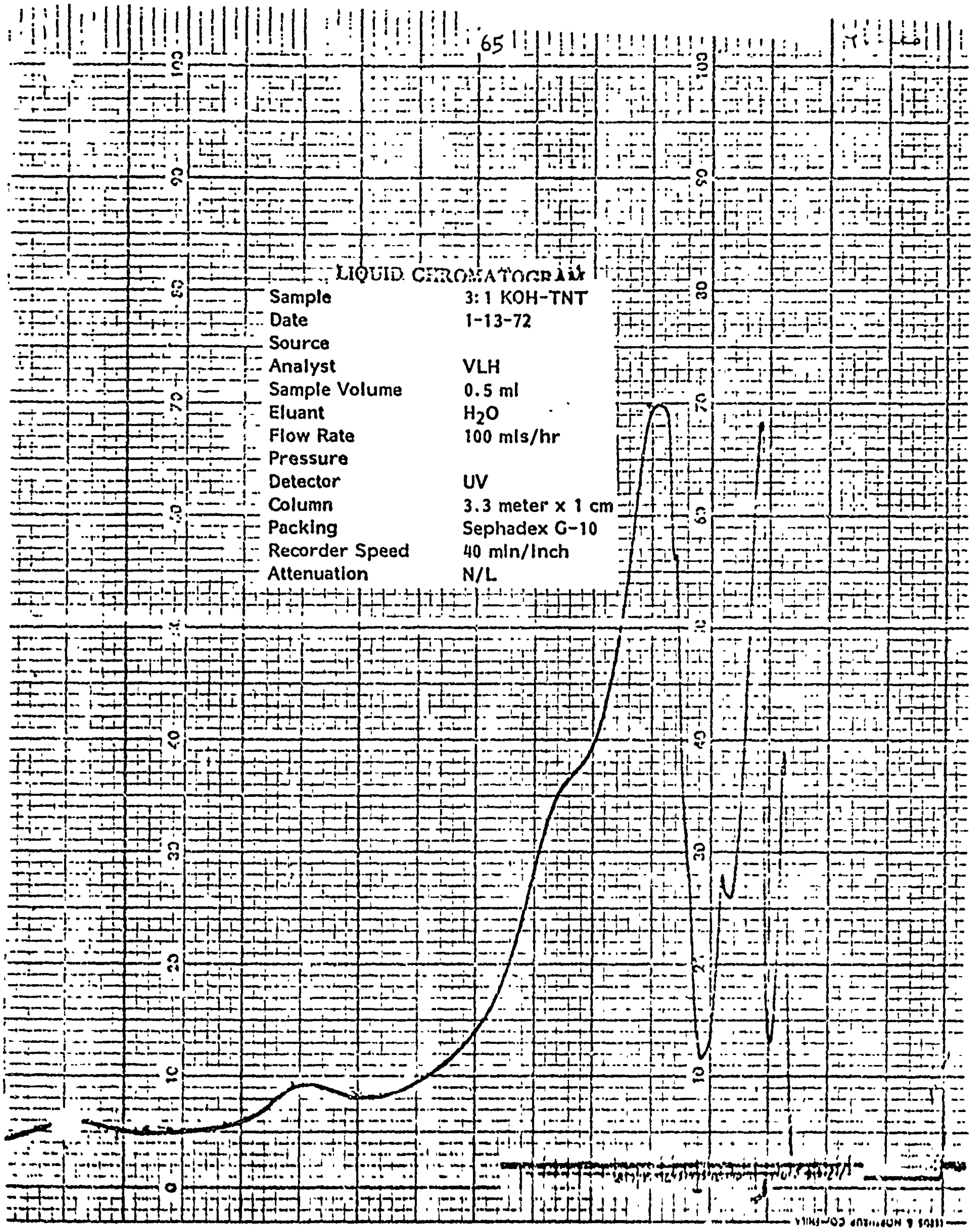
Figure XVIII. Infrared spectrum of freeze dried red TNT fraction from third peak to emerge from the liquid chromatograph.

collected for the peaks in the chromatogram were scanned by the ultraviolet spectrophotometer. The chromatogram in figure XIX shows the position of the fractions. The ultraviolet scans shown as figure XX have absorption plateaus at 250 and 200 millimicrons for fractions 6 and 19. Fractions 9 and 12 showed increasing absorption toward 200 millimicrons. Five liquid chromatograms are shown of the same material, all run within eight days of each other. Note the unfortunate variability of the runs in figures XIX, XXI, XXII and XXIII.

c. Sepharose 4B

Sepharose is manufactured from agarose. Agarose is a linear polysaccharide containing galatose units. This, of course, provides hydroxyl groups and the gelling properties have been attributed to hydrogen bonding. Gel filtration is still the means by which separation takes place just as it was with Sephadex. Sepharose is used mainly for separation of much higher molecular weight compounds than is Sephadex. The exclusion limit of Sepharose 4B is estimated by Pharmacia Fine Chemicals to be 3 to 4 million molecular weight. One property of Sepharose which must be remembered when constructing and operating columns is the variation of bed height with flow rate. The bed height can vary as much as 10%. This problem is eliminated by stabilizing the column at a high flow rate and using a plunger assembly in column construction.

Due to unavailability of the 254 millimicron UV monitor a recording UV-visible spectrophotometer was fitted with flow-



LIQUID CHROMATOGRAM

Sample	3:1 KOH-TNT
Date	1-13-72
Source	
Analyst	VLH
Sample Volume	0.5 ml
Eluant	H_2O
Flow Rate	100 mls/hr
Pressure	
Detector	UV
Column	3.3 meter x 1 cm
Packing	Sephadex G-10
Recorder Speed	40 min/inch
Attenuation	N/L

Figure XIX. Liquid chromatogram of red TNT

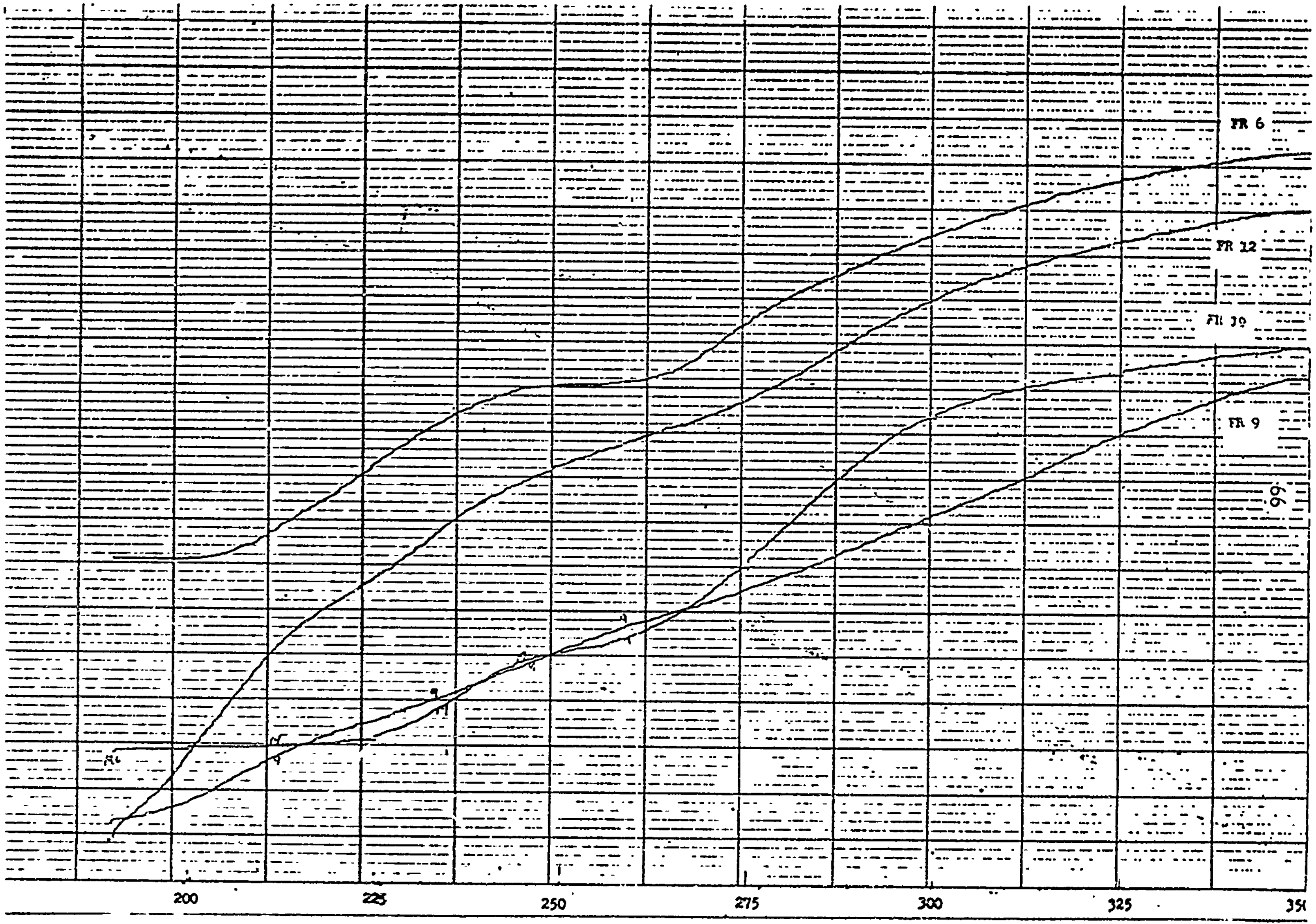
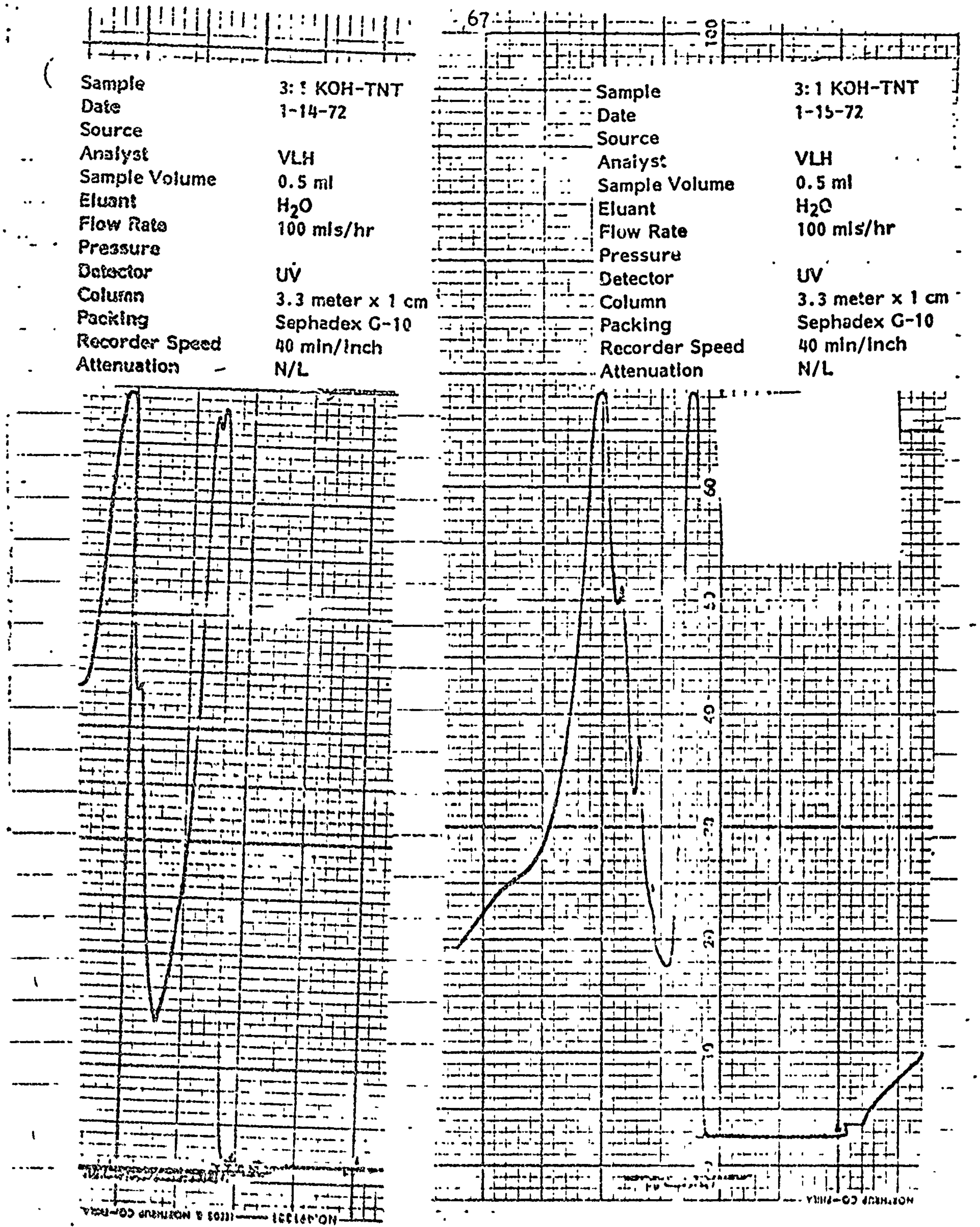


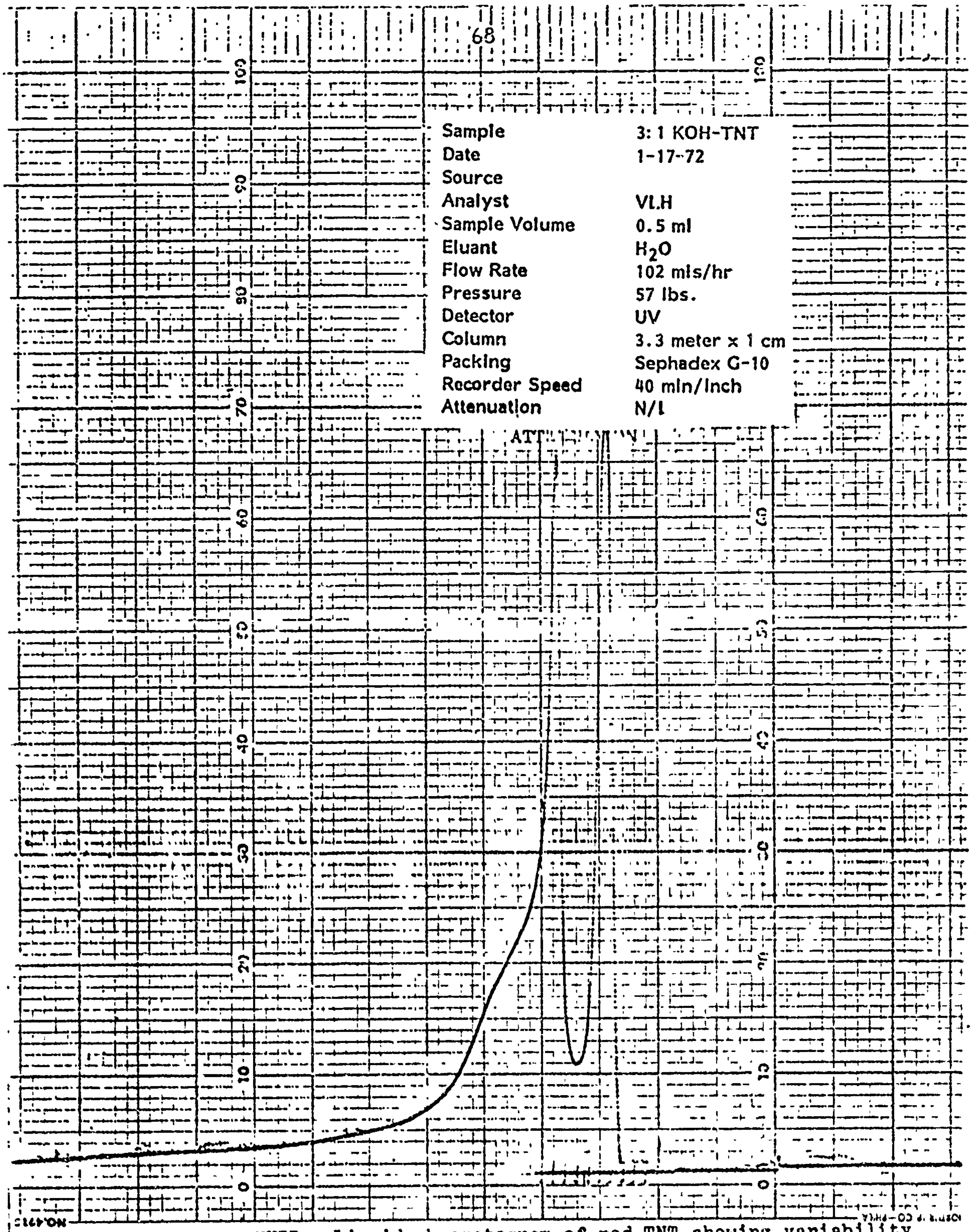
Figure XX. Ultraviolet spectrum of fractions from each peak in chromatogram shown as Figure XIX



Sample 3:1 KOH-TNT
Date 1-14-72
Source
Analyst VLH
Sample Volume 0.5 ml
Eluant H_2O
Flow Rate 100 mls/hr
Pressure
Detector UV
Column 3.3 meter x 1 cm
Packing Sephadex G-10
Recorder Speed 40 min/inch
Attenuation N/L

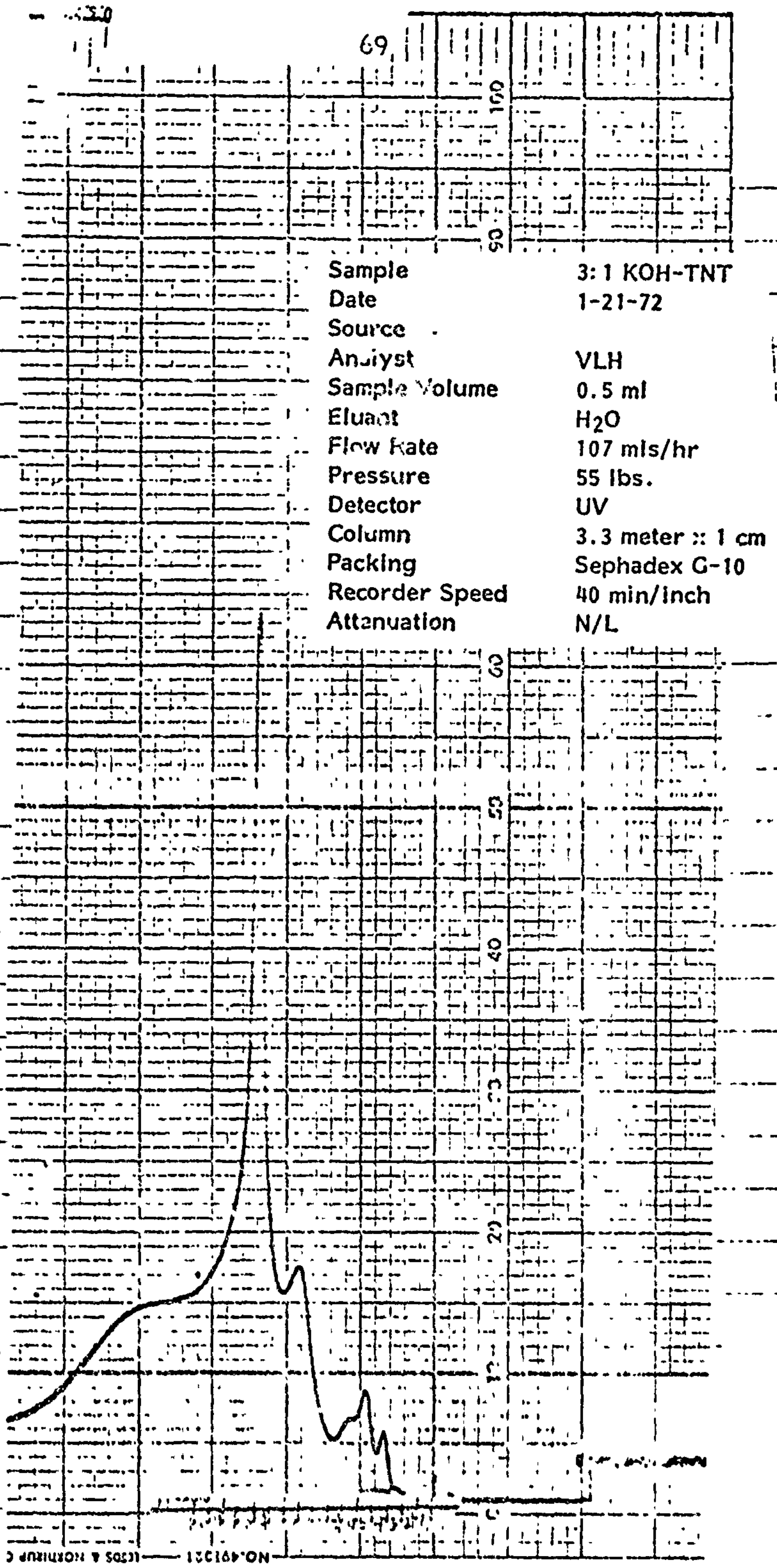
Sample 3:1 KOH-TNT
Date 1-15-72
Source
Analyst VLH
Sample Volume 0.5 ml
Eluant H_2O
Flow Rate 100 mls/hr
Pressure
Detector UV
Column 3.3 meter x 1 cm
Packing Sephadex G-10
Recorder Speed 40 min/inch
Attenuation N/L

Figure XXI. Liquid chromatogram of red TNT showing variability of each run



Sample	3:1 KOH-TNT
Date	1-17-72
Source	
Analyst	VLH
Sample Volume	0.5 ml
Eluant	H_2O
Flow Rate	102 mls/hr
Pressure	57 lbs.
Detector	UV
Column	3.3 meter x 1 cm
Packing	Sephadex G-10
Recorder Speed	40 min/inch
Attenuation	N/I

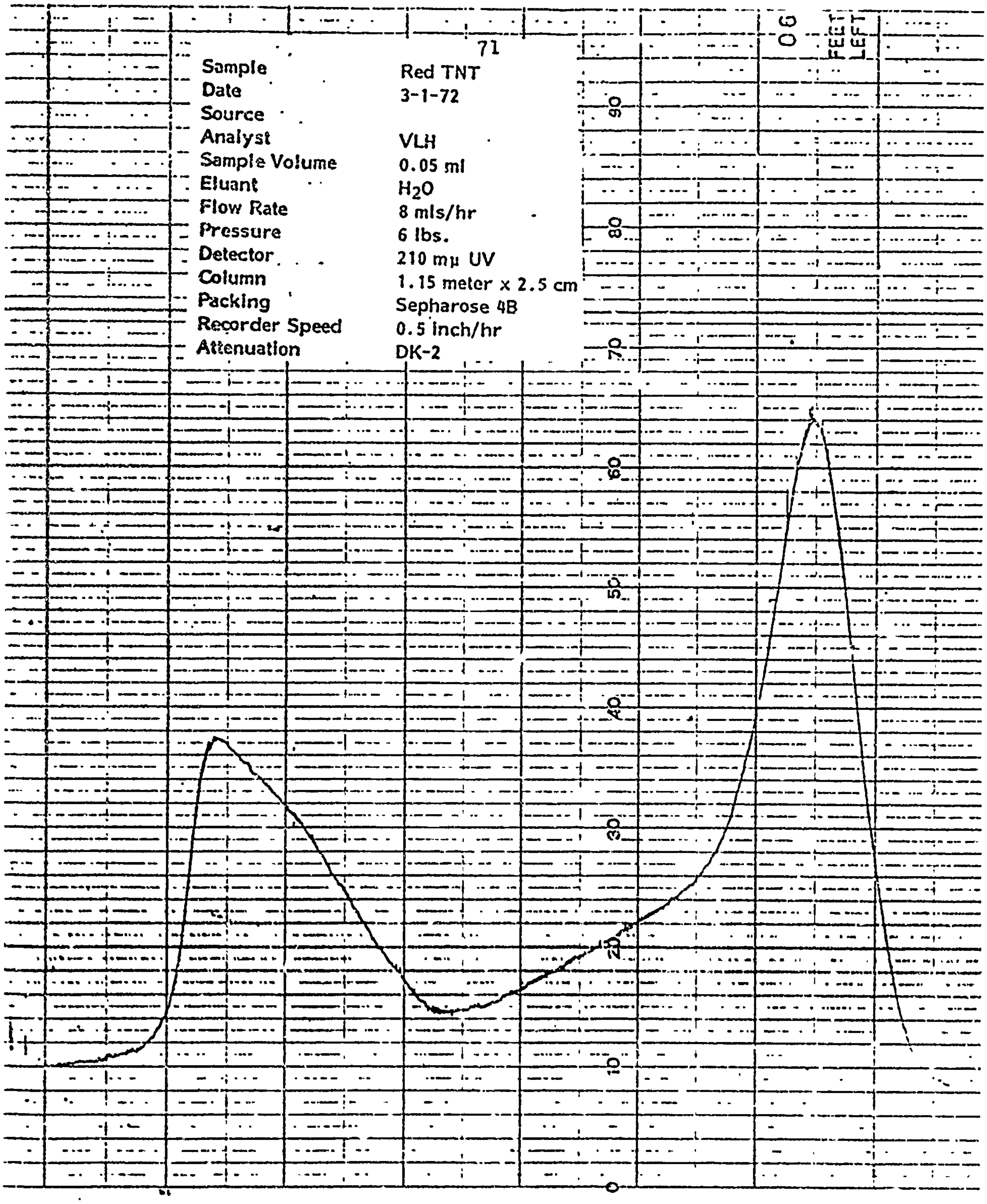
Figure XXII. Liquid chromatogram of red TNT showing variability of each run



Sample	3:1 KOH-TNT
Date	1-21-72
Source	
Analyst	VLH
Sample Volume	0.5 ml
Eluant	H_2O
Flow Rate	107 mls/hr
Pressure	55 lbs.
Detector	UV
Column	3.3 meter x 1 cm
Packing	Sephadex G-10
Recorder Speed	40 min/inch
Attenuation	N/L

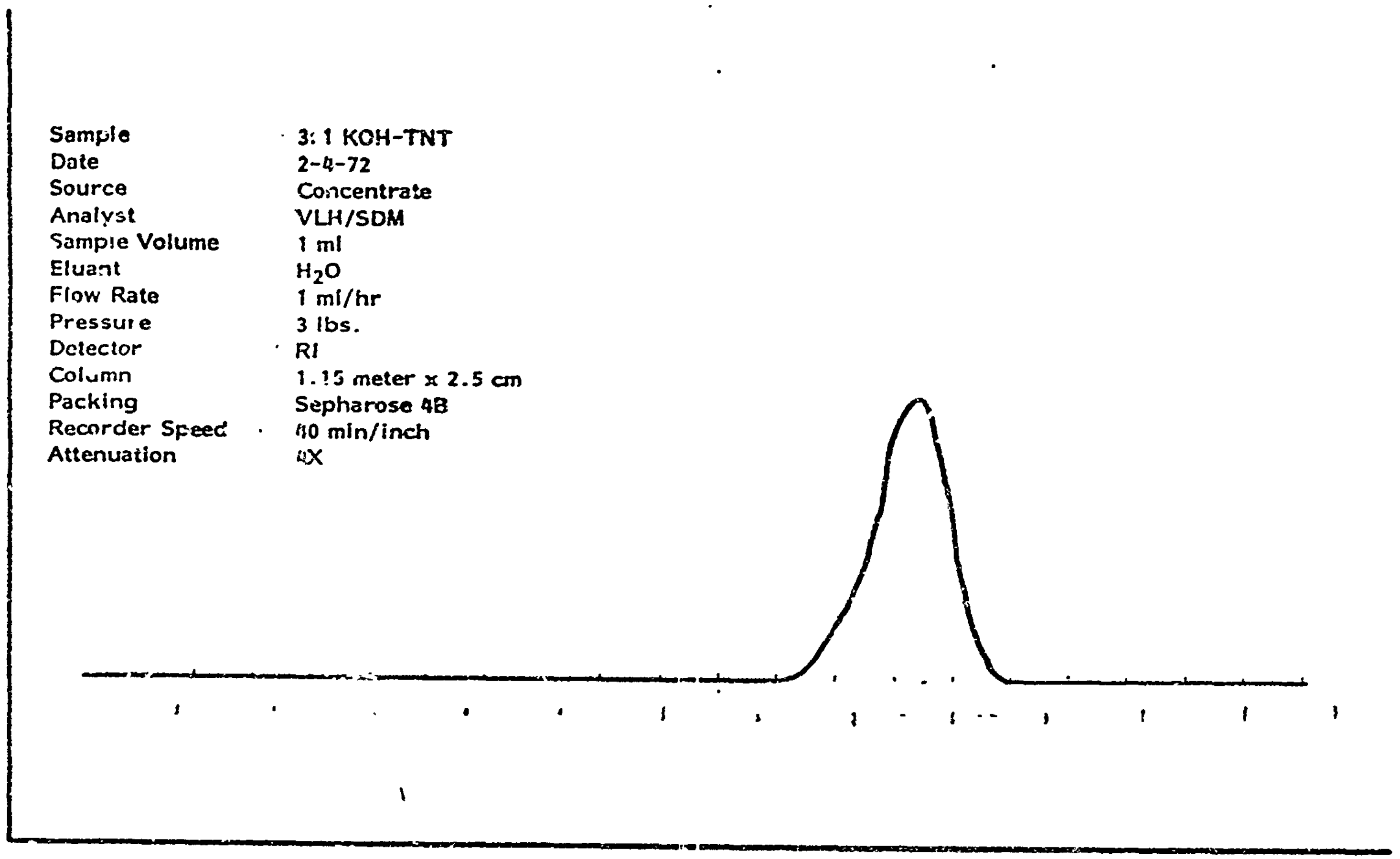
Figure XXIII. Liquid chromatogram of red TNT showing variability of each run through cells for use as an ultraviolet detector. The wavelength for detection could be set as desired, but the large volume of the flow-through cells cut down on resolution and sensitivity. Red TNT showed only two major peaks, as seen from figure XXIV. The first peak was collected and saved from several runs. Finally enough of peak one was available for elemental analysis. Duplicate runs were made on the elemental analyzer. One run gave 5.12% nitrogen, 28.91% carbon and 2.77% hydrogen. The second run gave 5.10% nitrogen, 28.75% carbon and 2.88% hydrogen.

The refractive index detector was used on a run which took nearly half a week to complete because of the one milliliter per hour flow rate. Fractions were collected. Only one peak appeared on the refractive index monitor recorder, as shown by figure XXV. A late peak was detected after shut down of the refractive index detector. Sodium hydroxide test and UV scan indicated this component (fraction 19) may have been TNT. Fractions 5, 12, 15 and 19 were scanned in the ultraviolet region. The scans are illustrated as figure XXVI. Fraction 5 was collected before components began to emerge. Fractions 12 and 15 are at the very heart of component emergence. Notice the relatively sharp absorption in the 210 millimicron region. Fraction 19, peaking around 225-230 millimicrons, probably indicates TNT. All fractions were measured for absorbance at 210 millimicrons and the results plotted. The outcome shown in figure XXVII was a flat peak in front of a larger peak. A later run (figure XXVIII) at higher flow rate sh wed some resolution



Sample	Red TNT
Date	3-1-72
Source	
Analyst	VLH
Sample Volume	0.05 ml
Eluant	H_2O
Flow Rate	8 mls/hr
Pressure	6 lbs.
Detector	210 mμ UV
Column	1.15 meter x 2.5 cm
Packing	Sepharose 4B
Recorder Speed	0.5 inch/hr
Attenuation	DK-2

Figure XXIV. Liquid chromatogram of red TNT using flow-through cells and Sepharose 4B packing



Sample	3:1 KOH-TNT
Date	2-4-72
Source	Concentrate
Analyst	VLH/SDM
Sample Volume	1 ml
Eluant	H_2O
Flow Rate	1 ml/hr
Pressure	3 lbs.
Detector	RI
Column	1.15 meter x 2.5 cm
Packing	Sepharose 4B
Recorder Speed	40 min/inch
Attenuation	4X

Figure XXV. Liquid chromatogram of red TNT using 1 ml/hr flow rate

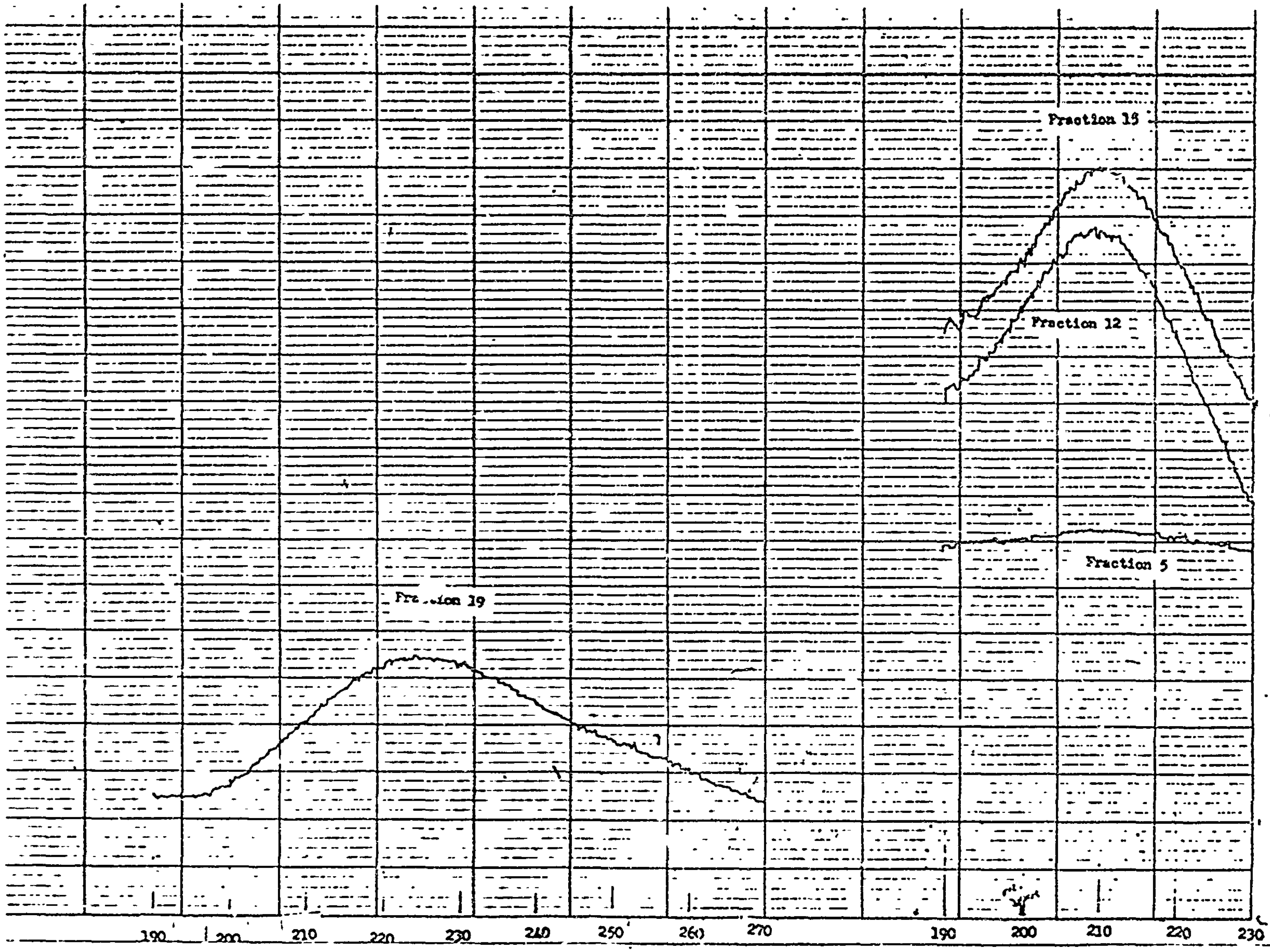
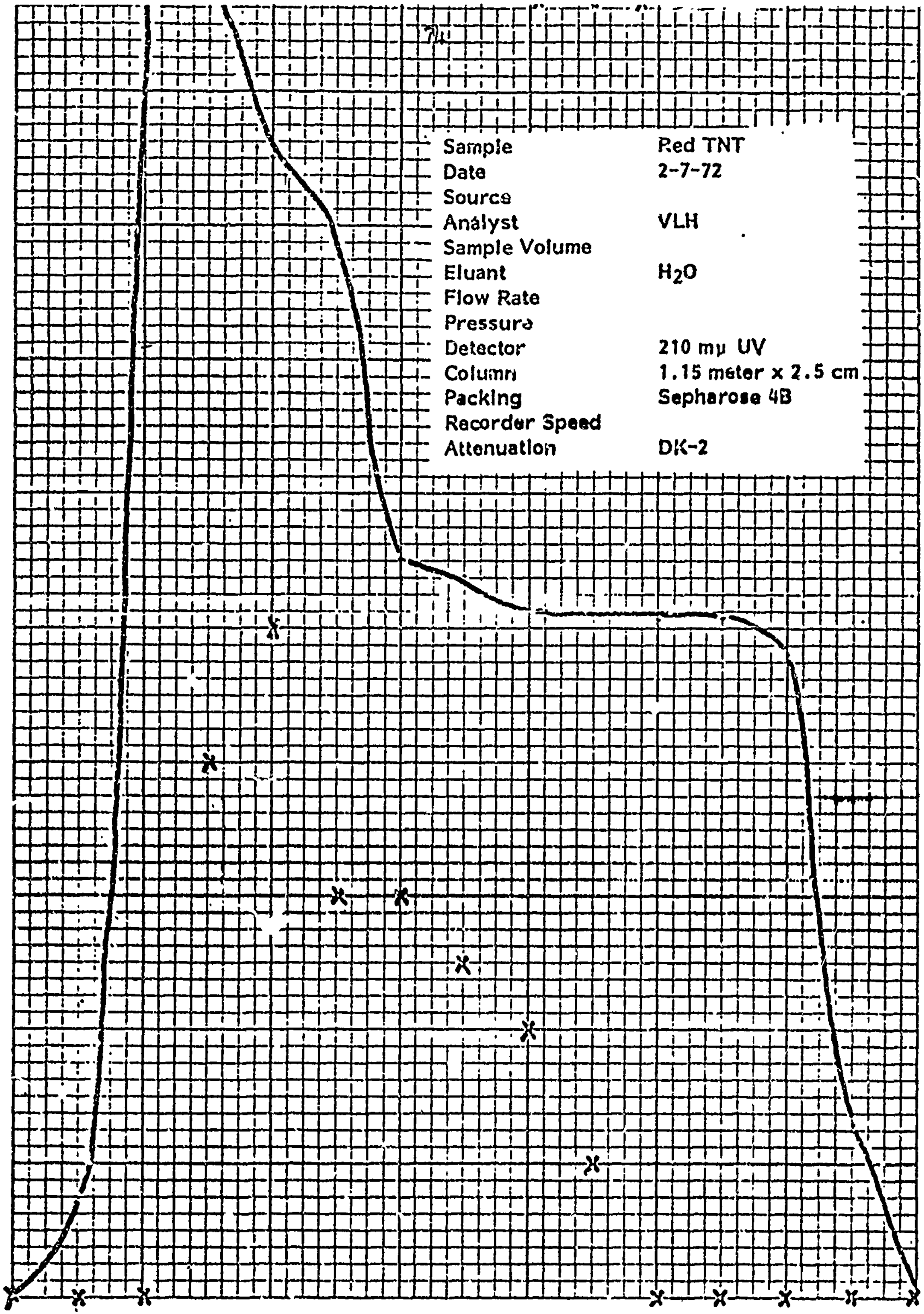


Figure XXVI. Ultraviolet spectrums of fractions collected from chromatogram illustrated in Figure XXV



Sample	Red TNT
Date	2-7-72
Source	
Analyst	VLH
Sample Volume	
Eluant	H_2O
Flow Rate	
Pressure	
Detector	210 mμ UV
Column	1.15 meter x 2.5 cm
Packing	Sepharose 4B
Recorder Speed	
Attenuation	DK-2

Figure XXVII. Response at 210 mu of fractions collected fr chromatogram shown in Figure XXV. (Nitrite is indicated.)

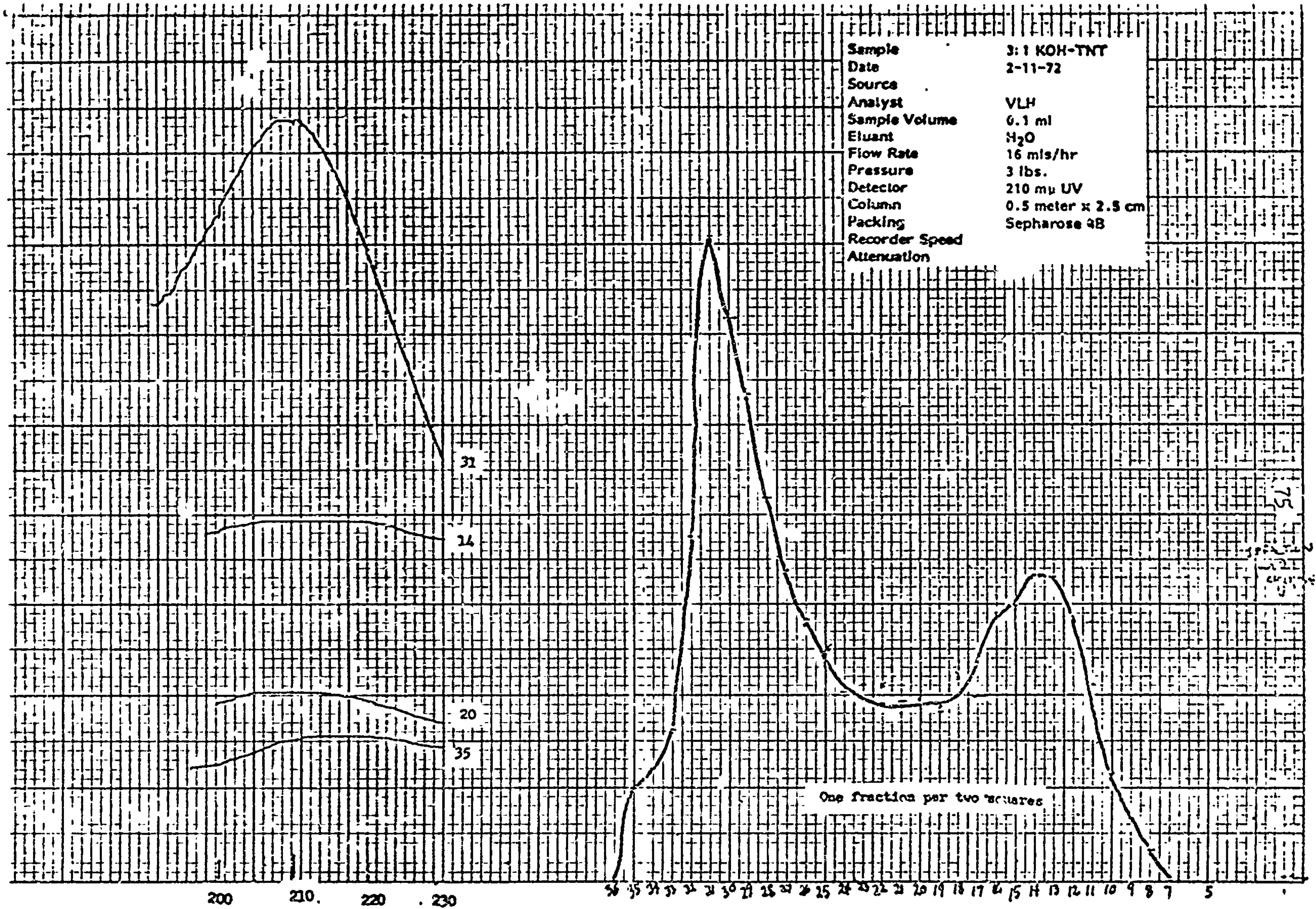


Figure XXVIII. quid chromatogram using 16 mls/hr and 210 mu detector of the two peaks. The second peak produces a sharp, strong absorption at 210 millimicrons.

d. Sepharose 6B

Manufacturer's specification data from Pharmacia Fine Chemicals are not yet available on Sepharose 6B because it is a very recent product. The information available mentions its exclusion limit is lower than Sepharose 4B, i. e. less than 3 to 4 million molecular weight. A column of Sepharose 6B 162.5 centimeters in length by 2.5 centimeters in diameter was prepared. Like Sephadex G-10 the chromatograms produced by Sepharose 6B were not reproducible. Indications were that it did a better job of separating the components of red TNT than did Sepharose 4B. It was slightly inferior to the performance of Sephadex G-10 with the exception that it did not permanently retain any colored component as the Sephadex G-10 did. Some of the chromatograms indicated as many as six components or more. The chromatogram in figure XXIX bears this out. The detector was a UV-visible spectrophotometer equipped with flow-through cells, the same system used for Sepharose 4P. The wavelength monitored was 254 millimicrons, so as to keep data consistent with previous results. In figure XXIX it can be seen that nitrite emergence does not coincide with potassium emergence. The emergence of nitrite seems to be rather erratic. As pointed out before, the nitrite does not always emerge with a corresponding peak as indicated by the UV monitor. Another chromatogram displayed in figure XXX indicates that the emergence of nitrite is less erratic;

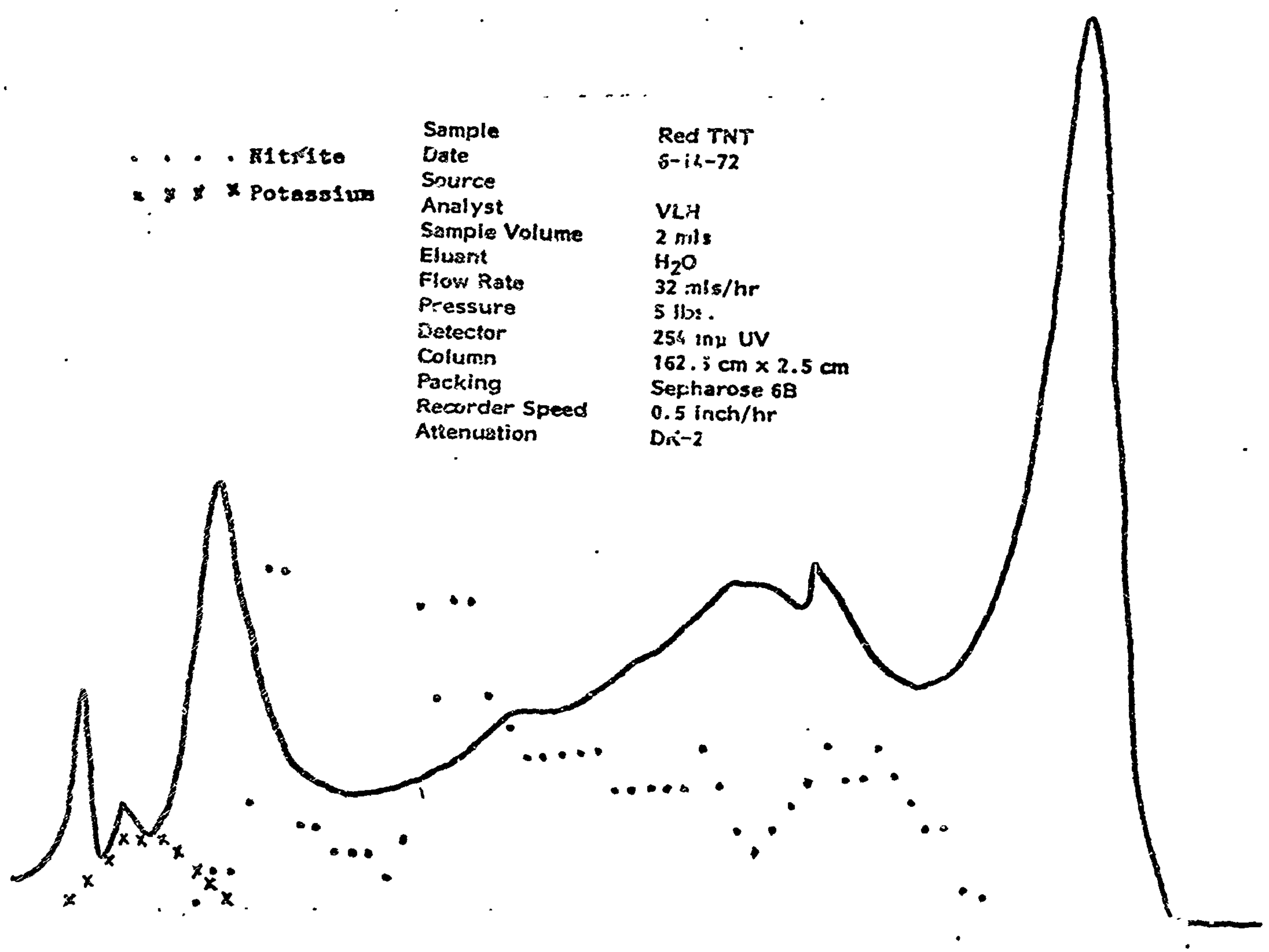


Figure XXIX. Liquid chromatogram using Sepharose 6B packing with potassium and nitrite emergence indicated

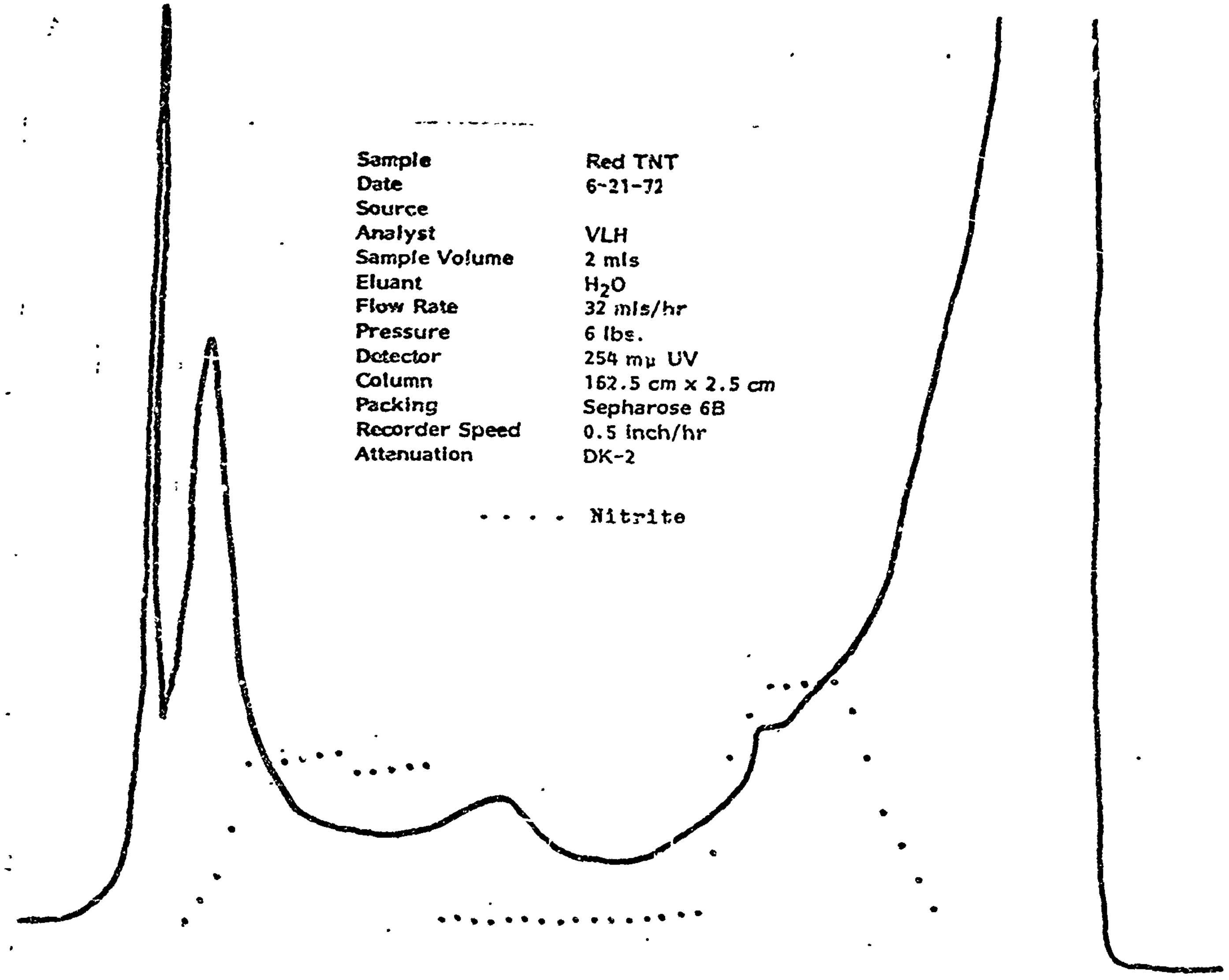
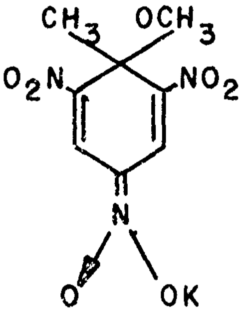


Figure XXX. Liquid chromatogram using Sepharose 6B packing showing two nitrite peaks in fact, it elutes as two separate peaks. It is not certain what this indicates. Perhaps the nitrite is associated with two different positively charged organic species.

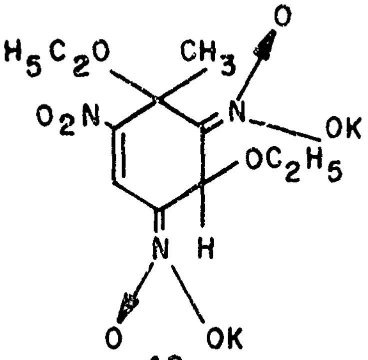
IV. DISCUSSION AND CONCLUSIONS

Urbanski[52] postulated a structure (47) for a product produced from TNT, methanol and potassium hydroxide. The structure is

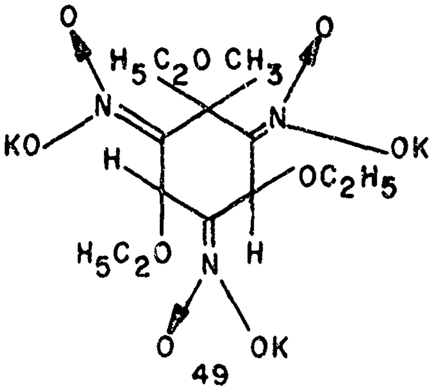


47

Likewise, the potassium alcoholate (ethanol) reaction with TNT supposedly would give (48) and (49).



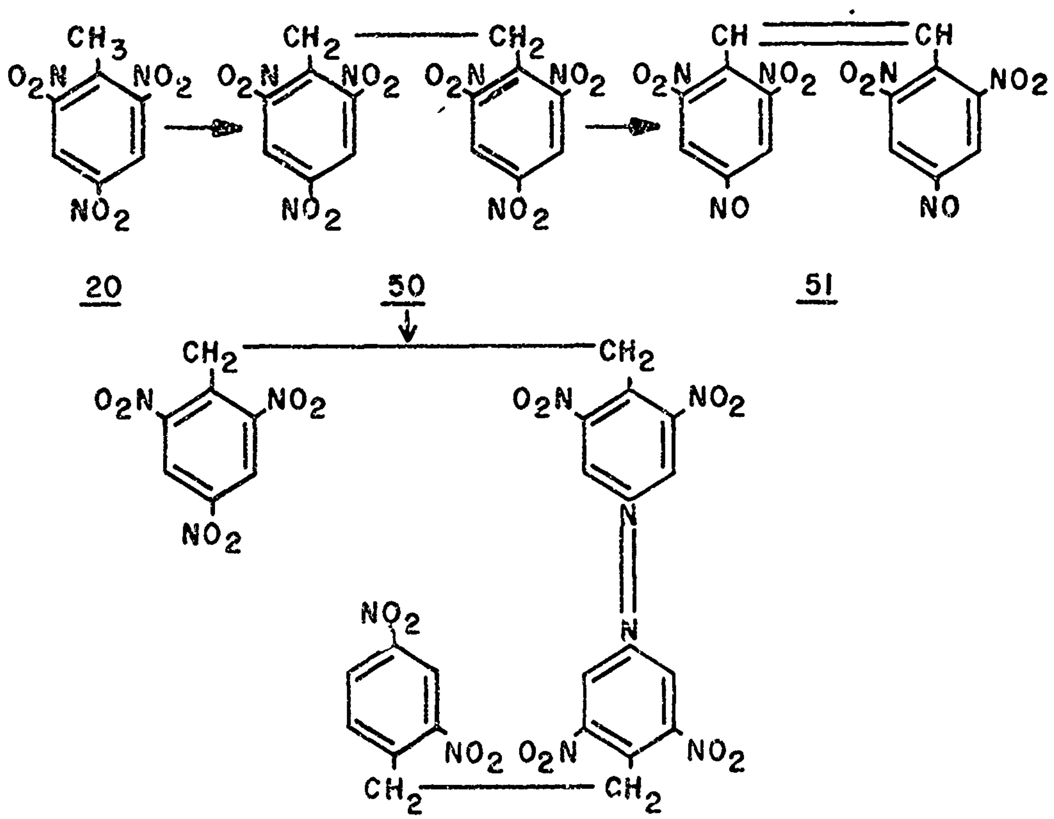
48



49

As can be seen structures (47), (48) and (49) correspond to a 1:1, 2:1 and 3:1 mole ratio of potassium alcoholate to TNT respectively.

Copisarow[53] proposes the following to take place in TNT-hydroxide reactions:



20 50 51

52

It seems unlikely that compounds with the structures (50), (51) and (52) are formed in the aqueous hydroxide reaction with TNT because of the high solubility of red TNT components in water. Compounds (50), (51) and (52) would not be expected to be very soluble in water due to long organic chain structure.

The infrared spectra generated from the red TNT components could not be matched with any compound in the reference files. Possible interpretation of the bands shown in figure XXI was possible with the help of the reference from Henry Feuers' volumes[30] and Conley's volume[54]. The spectra generated all have the familar OH band at 3400 cm^{-1}. This can be expected when potassium bromide is used for pelletizing the sample. Another band due to water appears around 1625 cm^{-1} and is always less intense

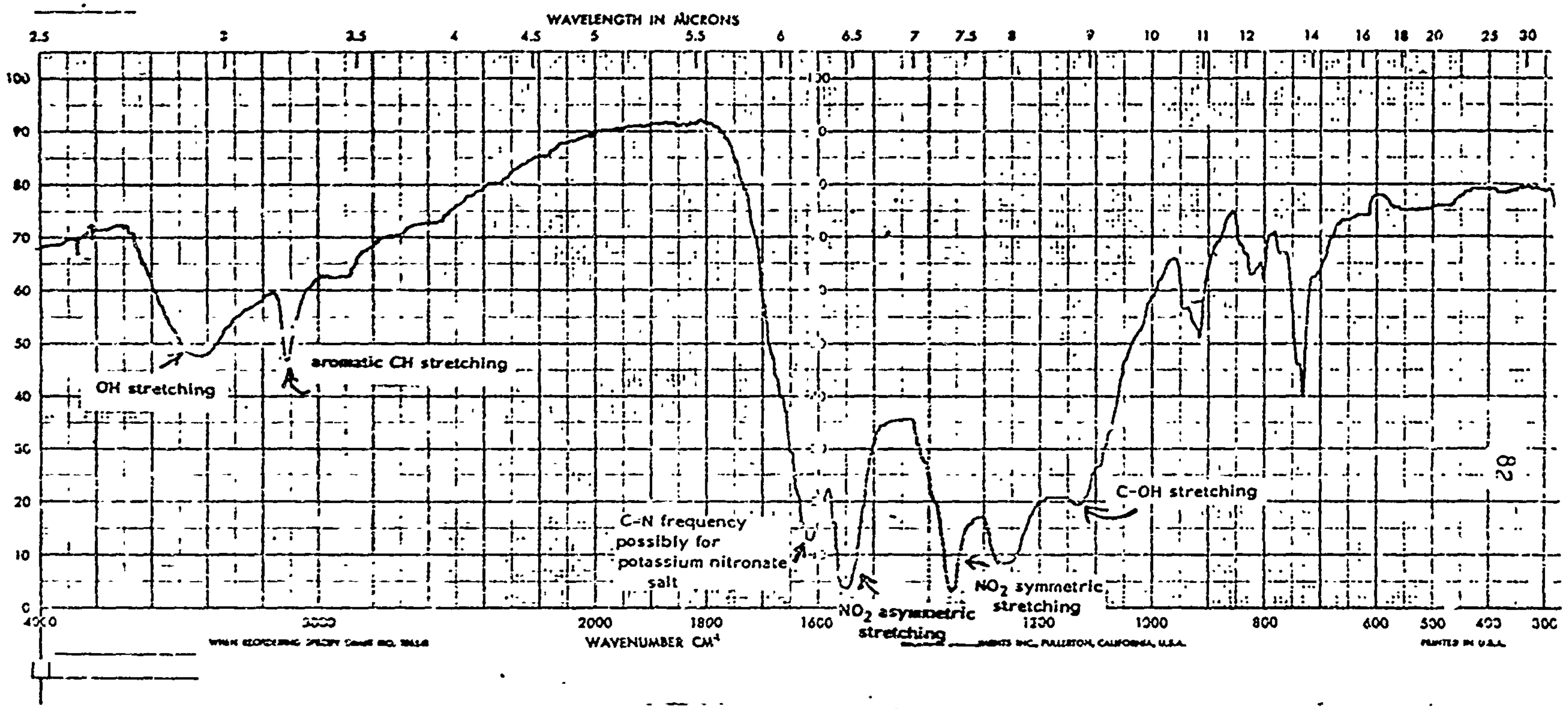
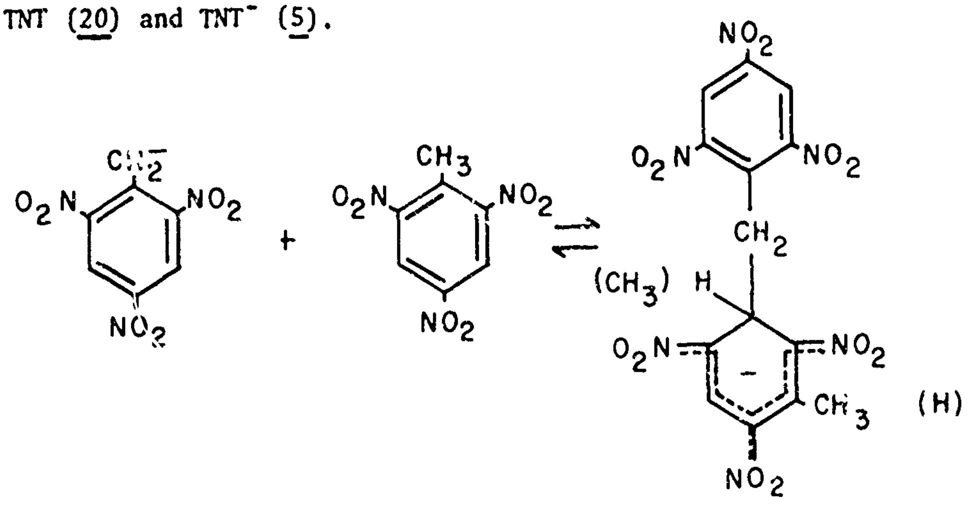


Figure XXVI. Infrared spectrum of red TNT with possible band assignments than the 3400 cm^{-1} band. The band appearing in many of the spectra at 1625 cm^{-1} is stronger than the 3400 cm^{-1} band; therefore, it is not due entirely to water. It is unlikely that the 3400 cm^{-1} band is due entirely to moisture absorption by the potassium bromide. All precautions were taken to keep moisture pick up minimal. The die parts and grinding vials were always kept under a heat lamp. When micro pellets were made the pellet holder was also kept hot. The potassium bromide was kept in a desiccator at all times. Some samples were mixed with potassium bromide in a water solution and then freeze dried. The sample compartment of the Beckman IR-20A is enclosed and purged with dry nitrogen. Even with these precautions the OH band at 3400 cm^{-1} still persisted. It is not unreasonable to assign this band to hydroxy groups that are attached to the aromatic ring at one or more positions.

The band in the 1600-1650 cm^{-1} region could be due to C=N from a nitronate salt. The C=N absorption is said to occur in the region 1587-1605 cm^{-1}. Figure XXXI, which is a spectrum of a flash evaporated sample from reaction of 1:1 KOH-TNT, shows bands at 1540 cm^{-1} and 1350 cm^{-1}. These bands are the asymmetric and symmetric stretching of the nitro group respectively. A carbon-oxygen stretching vibration from the C-OH bond occurs at 1200-1000 cm^{-1}. A band which persisted in nearly all the infrared spectra was the 1380 cm^{-1} band. No good explanation of this band could be made. The C-N stretching frequency of a nitro substituted aromatic compound has been assigned to the region 1360-1250 cm^{-1} and is due to conjugation of the electron pair of the nitrogen atom to the ring, imparting double bond character to the C-N bond. Some authors[55, 56] mention that the whereabouts of this C-N band is indefinite. Another possible identification of the 1380 cm^{-1} band occurring in the red TNT spectra is nitrate. Sometimes the symmetric vibration of the nitro group occurs at about 1360 cm^{-1}, but an asymmetric stretching band should also be visible at 1530-1560 cm^{-1}. In most of the spectra the 1380 cm^{-1} band is not accompanied by any band in the 1530-1560 cm^{-1} region. It is not likely that symmetric and asymmetric frequencies of the nitro group could be shifted to remote positions such as 1380 cm^{-1} and 1610 cm^{-1}. A few of the spectra showed a strong absorption at 1270 cm^{-1}. This band can definitely be assigned to the presence of nitrite. This assignment is definite because nitrite ions were detected by wet chemical means in some of the liquid chromatograph fractions.

Bands in the ultraviolet region can be indicative of particular species being present. It must be remembered that many different compounds have bands in the same ultraviolet region. Trinitrotoluene absorbs at about 233 millimicrons, and references in the literature[31] indicate that aliphatic nitronic acids absorb at 220-230 millimicrons, while nitronate anions absorb about 10 millimicrons higher. Components of red TNT absorb strongly at 208-210 millimicrons. A specific reference to the nitronic acid of mononitrobenzene was cited previously[31]. It absorbed at 284 millimicrons, its sodium salt at 294 millimicrons. The only close match of the red TNT component with substances described in the literature is the nitronate anion, but even here the experimental results were 20 to 30 millimicrons too low. One component separated from the liquid chromatograph and scanned in the ultraviolet did absorb in the 225-240 millimicron region. This is where Nielsen[31] says the nitronate anion absorbs.

As was mentioned before, the spectrum of TNT in basic methanol-water (90-10) is very similar to Bernasconi's[11] calculated spectrum of TNT^- in methanol. The spectrum has absorptions at 510 and 370 millimicrons. The 510 millimicron band is barely perceptible in the 100% aqueous system. Since the 370 millimicron band is weaker it could be hidden in the envelop of the 460 millimicron band. The TNT anion may be present in the purely aqueous system as a minor and probably short lived species. Bernasconi[11] suggested the following reaction scheme involving TNT (20) and TNT^- (5).

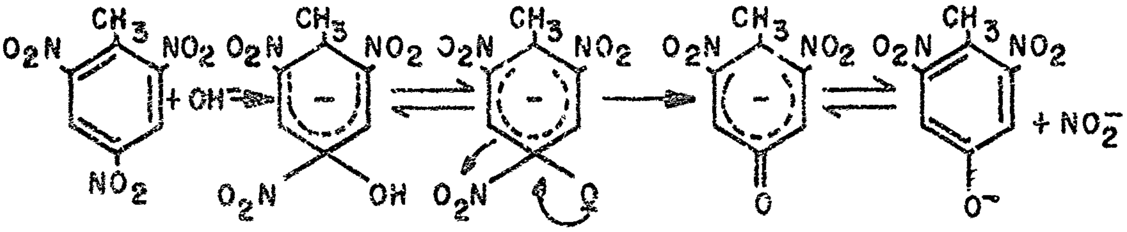


5 20 53

The product (53) has been named a Janovsky complex and Bernasconi[11] gives a calculated spectrum for this complex in different solvent systems. Although purely aqueous media was not one of the solvent systems for the calculated spectrum, the absorption at 460 millimicrons may be more than just coincidental with the observed 460 millimicron band found in 100% aqueous media. The band shifts during the course of the base reaction with TNT. It could be possible that the Janovsky complex (53) is formed immediately upon addition of base to TNT in water. The reaction could be so fast that the evidence for TNT^- is barely perceptible. With time the Janovsky complex may change to another compound or compounds. It is the latter compounds that all other analytical techniques are detecting. Other than the UV-visible scans no other evidence can substantiate this line of reasoning.

Various things can be gleaned from the observations made by liquid chromatography. For instance, one component was permanently retained on Sephadex G-10. This would imply that the component molecule was small enough to enter the Sephadex bead and so highly polar that it was held within the bead by the hydroxyl groups of the polysaccharide chains. It is believed that the red TNT components contain hydroxyl groups on the ring. If this is the case then hydrogen bonding could occur between the hydroxyl groups of red TNT and Sephadex. The presence of a peak with a leading edge is not a common occurrence in chromatography. As was explained earlier (page 55, this thesis) this condition is caused by the component having a stronger attraction for itself than for the column packing, in this case Sephadex. Indications are this component is a potassium salt because of the detection of potassium ions associated with this peak. This type of peak asymmetry is common with strongly polar materials. The nature of these compounds are such that a positive charge can exist at the site where the methyl group is attached or at the unoccupied sites on the ring. Likewise, negative charges occur on the oxygens of the nitro groups that are attached to the ring. Potassium could be associated with the nitro groups and hydroxyl ions could be associated with the positive sites on the ring. The negative site of one ring entity could attach to the positive site of another ring to give the mutual attraction necessary to cause the peak asymmetry observed. This association could last just long enough to cause the skewed peak.

Nitrite ions were detected in the fractions from liquid chromatographic runs. As was suggested by Gold and Rochester[57] a photochemical attack on trinitrobenzene in the presence of alkali can cause a nitro group to be lost as a nitrite ion. No precautions were taken with the TNT-water-alkali mixture to prevent photochemical reactions from taking place. The following reaction could occur for TNT (20):



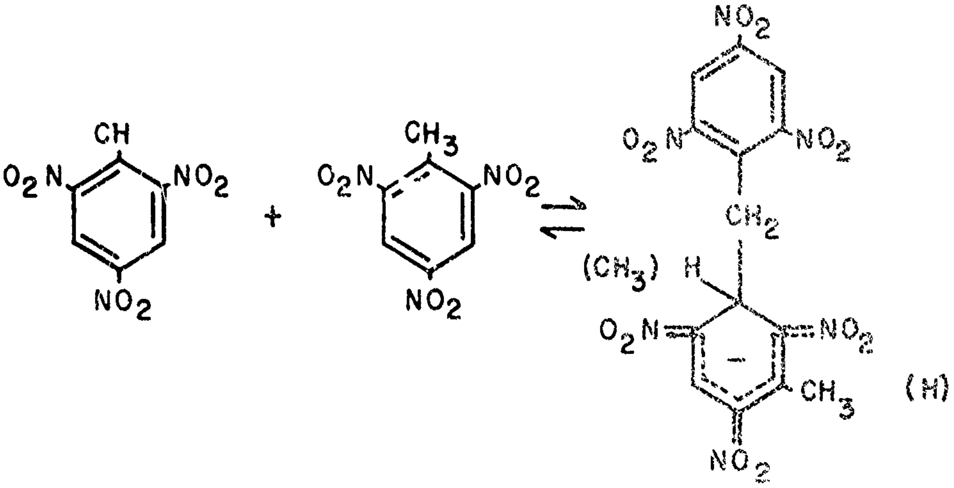
20 54 55 56 57

Elemental analysis was conducted on two components of red TNT. Percent carbon, hydrogen and nitrogen were obtained. One run was made on the fourth peak to emerge from the Sephadex G-10 column. Two runs were made on the first peak to emerge from the Sepharose 4B column. The water fractions containing these components were collected from several chromatographic runs, combined and freeze dried. The dry residue was weighed and analyzed in a commercial elemental analyzer. Below is a tabulation of the results:

Sample	% N	% C	% H
Red TNT Peak 4, Sephadex G-10	7.12	20.51	1.82
Red TNT Peak 1, Sepharose 4B	5.12	28.91	2.77
Red TNT Peak 1, Sepharose 4B	5.10	28.75	2.88

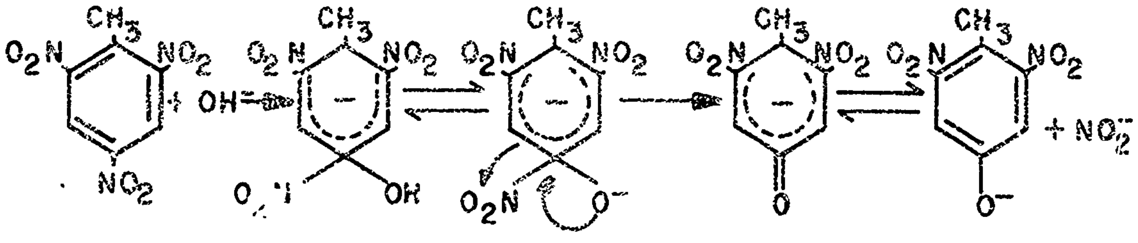
This analysis shows a nitrogen to carbon to hydrogen ratio for the runs as tabulated above as 2:6.7:7.2, 1:6.6:7.6 and 1:6.6:7.9. The quantity of nitrogen in these materials is even less than the nitrogen for the tripotassium nitronate salt. A decrease in nitrogen would not be unexpected in light of liberation of nitrite ion which was detected by liquid chromatography, wet chemical test and infrared spectroscopy. One observation not previously mentioned was the detection of ammonia from a flash evaporated portion that had been stoppered in a flask for a considerable time. Gold and Rochester[57] mention ammonia liberation during alkali reaction with trinitrobenzene. They say a reduction product formed could reduce the nitrite ion to liberate ammonia. The compound 3,5-dinitroaniline was mentioned as one that could react rapidly with alkali to liberate ammonia. Since nitrite ion has been detected in the formation of red TNT, then possibly some of the intermediate products could cause reduction of nitrite with liberation of ammonia. The flash evaporated material was not completely dry, probably because of residual alkali which, if concentrated, could provide the conditions for eventual ammonia formation. This could lead to compounds with low nitrogen content.

The proposed structures of compounds formed and reaction paths followed can be reasoned from literature references as well as experimental evidence. Due to similiarity to Bernasconi's[11] visible spectra it is concluded that the TNT anion (5), though a very transient species, could exist in 100% aqueous media and could attach to TNT (20) to form a Janovsky complex (53) by the following scheme:



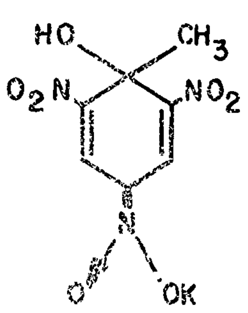
5 20 53

Since nitrite ions were detected in the reaction products and in view of Gold and Rochester's[57] description of a photochemical attack on trinitrobenzene in the presence of alkali to liberate nitrite the following reaction mechanism is concluded as possibly occurring with TNT and alkali:

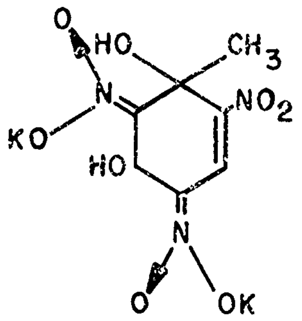


20 54 55 56 57

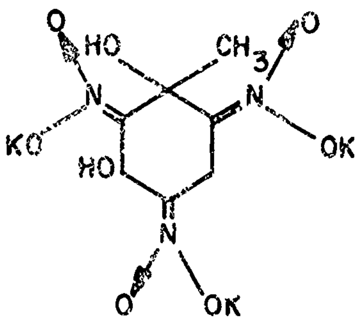
The structures supported by infrared and UV-visible spectrophotometric data as well as observed behavior on the liquid chromatographic column are as follows:



44



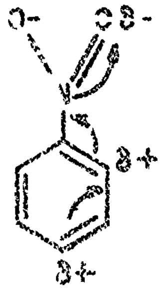
45



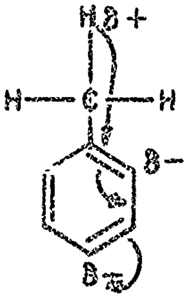
46

The methyl group is small and does not crowd the nearby nitro groups. If crowding occurred then the nitro group could leave the ring and be replaced by another substituent. Only "mild" conditions would be required for such a replacement.

The three potassium nitronate salts (44), (45) and (46) would be expected to form on the basis of electron density distribution in the TNT molecule. The nitro group is electron withdrawing and produces a negative inductive effect, -I (see page 13, this thesis) which reduces the electron density at each nuclear carbon. The nitro group also displays a mesomeric effect, -M (see page 13, this thesis) which causes a further electron withdrawal especially from ortho and para carbons. In TNT this would cause reduced electron density on the unsubstituted nuclear carbons as well as the nuclear carbon occupied by the methyl group. The methyl group, however, is electron donating and produces a positive inductive effect, +I as well as a positive mesomeric effect, +M. The polarization of the aromatic ring for nitro and methyl groups are depicted as (58) and (59).



58



59

In TNT both groups are present on the aromatic ring. However, from the polarization models (58) and (59) it can be seen that the methyl group and nitro groups, if ortho and/or para to each other, would combine their effects. This condition exists in TNT. A deficiency in electron density would exist at the unoccupied nuclear carbons as well as the nuclear carbon occupied by the methyl group. A nucleophilic group such as hydroxyl which would seek to share its electrons would attach at the sites of lowest electron density.

LITERATURE REFERENCES

1. V. Meyer, Ber. 65, 319 (1889).

2. J. Meisenheimer, Annalen 323, 205 (1902).

3. A. Hantzsch and E. Wechsler, Annalen, 325, 226 (1902).

4. A. Hantzsch and H. Kissel, Ber. 32, 3137 (1899).

5. T. Urbanski, Chemistry and Technology of Explosives, Vol. 1, Macmillan Company, New York, New York, 1964, p 260.

6. T. Urbanski, Chemistry and Technology of Explosives, Vol. 1, Macmillan Company, New York, New York, 1964, p 261.

7. T. Urbanski, Chemistry and Technology of Explosives, Vol. 1, Macmillan Company, New York, New York, 1964, pp 330-333.

8. E. F. Caldin and G. Long, Proc. Roy. Soc. 263 (1955).

9. A. Muller, Deut. Parfum., Ztg. 27, 107-108, 155-156 (1941); Chem. Zentr. I, 1442 (1942).

10. W. Zimmermann, Thesis, Bonn, 1936, p 14.

11. C. F. Bernasconi, J. Org. Chem., 36, 1671 (1971).

12. K. L. Servis, J. Amer. Chem. Soc., 89, 1508 (1967).

13. M. R. Crampton, Advan. Phys. Org. Chem. 7, 211 (1969).

14. J. B. Ainscough and E. F. Caldin, J. Chem. Soc. 2546 (1956).

15. J. V. Janovsky and L. Erb, Ber., 19, 2155 (1886).

16. C. F. Bernasconi and R. G. Bergstrom, J. Org. Chem. 36, 1325 (1971).

17. A. R. Norris, Can. J. Chem., 45, 175 (1967).

18. C. Krauz and A. Koci, Chemicky Obzor, 23, 81-85, Prague, May 30, 1948.

19. V. Gold and C. H. Rochester, J. Chem. Soc., 1717-1721 (1964).

20. H. Feuer, The Chemistry of the Nitro and Nitroso Groups, Interscience, New York, Part 2, 1970, pp 329-384.

21. G. Brieglieb, Elektronen-Donator-Acceptor-Komplexe, Springer Verlag, Berlin, 1961.

22. M. R. Crampton and V. Gold, J. Chem. Soc. 4293 (1964).

23. T. Abe, Bull. Chem. Soc. Japan, 31, 904 (1958).

24. H. Feuer, The Chemistry of the Nitro and Nitroso Groups, Interscience, New York, Part 2, 1970, pp 49-73.

25. E. Noelting, Chem. Ber. 9, 1797 (1876).

26. H. S. Fry, Z Phys. Chem. 76, 385, 396, 591 (1911); J. Amer. Chem. Soc. 34, 664 (1912); ibid. 36, 248, 1035 (1914).

27. D. Vorlander, Chem. Ber., 52, 263 (1919) ibid. 58, 1293 (1925).

28. A. I. Titov, Organicheskie Poluprodukty i Krasiteli, Vol. 2, ed. A. I. Korolev, P 46, Goskhimizdat, Moskva 1961.

29. R. O. C. Norman and G. K. Radda, J. Chem. Soc. 3610 (1961).

30. H. Feuer, The Chemistry of the Nitro and Nitroso Groups, Interscience, New York, Part 1, 1969, pp 79-135.

31. H. Feuer, The Chemistry of the Nitro and Nitroso Groups, Interscience, New York, Part 1, 1969, pp 349-486.

32. H. Feuer, The Chemistry of the Nitro and Nitroso Groups, Interscience, New York, Part 1, 1969, pp 487-612.

33. D. H. Rosenblatt, G. E. Lauterbach and G. T. Davis, Water Pollution Problems Arising From TNT Manufacture, A Survey, EASP 100-94, March 1971.

34. C. F. Bernasconi, J. Amer, Chem. Soc. 92, 1, 129-137 (1970).

35. J. F. Bunnett, Quarterly Reviews (London) 12, 1 (1958).

36. J. B. Ainscough and E. F. Caldin, J. Chem. Soc. (London) 2528-2546 (1956).

37. R. C. Farmer, J. Chem. Soc. (London) 3425-3430 (1959).

38. P. Karrer, Organic Chemistry, Elsevier Publishing Co., Inc., New York 1947, p 408.

39. N. V. Sidgwick, The Organic Chemistry of Nitrogen, Oxford University Press, 1966, pp 396-397.

40. C. F. Bernasconi, J. Amer. Chem. Soc., 92, 4682 (1970).

41. C. F. Bernasconi, J. Amer. Chem. Soc., 90, 4982 (1968).

42. G. A. Russell and E. G. Janzen, J. Amer. Chem. Soc., 89, 300 (1967).

43. R. Foster and D. Ll. Hammick, J. Chem. Soc., (London) 2153 (1954).

44. N. V. Sidgwick, The Organic Chemistry of Nitrogen, Oxford University Press, London, 1937, p 260.

45. E. Buncel, A. R. Norris and K. E. Russell, Quarterly Reviews 22, 123 (1968).

46. E. F. Caldin and G. Long, Proc. Roy. Soc., 228, 263 (1955).

47. D. G. Gehring, TNT Analytical Studies, RE-68-24, E. I. du Pont de Nemours and Company Eastern Laboratory, Gibbstown, New Jersey, July 5, 1968.

48. T. Urbanski, Chemistry and Technology of Explosives, Vol. 1, Macmillan Company, New York, New York, 1964, p 300.

49. J. L. Mulder and F. A. Buytenhuys, J. Chrom. 51, 459-477 (1970).

50. S. D. Maegerlein, private communication.

51. J. M. Goodson, V. Distefano and J. C. Smith, J. Chrom. 54, 43-53 (1971).

52. T. Urbanski, Chemistry and Technology of Explosives, Vol. 1, Macmillan Company, New York, New York, 1964, p 301.

53. M. Copisarow, Chem. News 112, 283 (1915).

54. R. T. Conley, Infrared Spectroscopy, Allyn and Bacon, Inc., Boston, Mass., 1966.

55. J. P. Brown, J. Amer. Chem. Soc., 77, 6341 (1955).

56. R. D. Kross and V. A. Fassel, J. Amer. Chem. Soc. 78, 4225 (1956).

57. V. Gold and C. H. Rochester, J. Chem. Soc., 1710-1716 (1964).