Military Technical College
Kobry Elkobbah, Cairo,
Egypt.

C.E.E. 2006

3rd International Conference
On
Chemical & Environmental
Engineering

PREPARATION AND SENSITIVITY CHARACTERISTICS OF 3-NITRO-1, 2, 4-TRIAZOL-5-ONE (NTO) –BASED CASTED EXPLOSIVE FORMULATIONS

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ABSTRACT

Different explosive formulations based on 3-Nitro-1, 2, 4-triazol-5-one (NTO), which is an extremely insensitive explosive, were prepared by casting with Trinitrotoluene (TNT) or Polyurethane (PU) to avoid casting problems originating from the high melting point of NTO. Synthesis of NTO was carried out by two consecutive reactions; condensation reaction of semicarbazide hydrochloride with formic acid to produce 1, 2, 4-triazol-5-one (TO), then nitration for the prepared (TO) with nitric acid. The obtained products from both reaction steps were characterized by the determination of melting point, infrared spectroscopy, and measurement of some explosive characteristics (Sensitivity to impact, friction, ignition temperature and delay of ignition). Different mixtures of NTO/TNT and NTO/PU were studied theoretically using a computer program. The obtained results of explosive performance parameters were utilized to select the explosive mixtures (NTO/TNT 65:35, NTO/PU 88:12) to be prepared and tested. Sensitivity to impact of TNT, prepared NTO and candidate formulations (NTO/PU 88:12, NTO/TNT 65:35) measured and compared together. Formulations based on NTO/PU have lowest sensitivity to impact (36 joule). The ignition temperatures of NTO/TNT (65:35) and for (NTO/PU) (88:12) explosive formulations were markedly less than that of pure TNT and pure NTO.

The obtained results of explosive performance parameters were used to determine the candidate explosive mixtures for future practical applications and work to explore the possible application of NTO in insensitive munitions (IM) compliant explosives.

KEY WORDS

NTO, TNT, PU, Sensitivity to impact, ignition temperature,

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ABBREVIATIONS

BAMO	Poly(3,3-bis azido methyl oxetane)
DOZ	Dioctyl azelate
HMDI	Hexamethylene di-isocyanate
HTPB	Hydroxy terminated polybutadiene
MAPO	Methyl aziridinyl phosphine oxide
NTO	3-Nitro – 1,2,4- triazol- 5- one
PBXs	Plastic bonded explosives
PU	Polyurethane
RDX	Cyclotrimethylenetrinitramine
TATB	1,3,5 triamino 2,4,6 Trinitrobenzene
TNT	2,4,6 Trinitrotoluene
TO	1, 2, 4-triazol-5-one

1. INTRODUCTION

Defense forces around the world are adopting Insensitive Munitions (IM), to minimize the response of ordnance items to accidental stimuli, thus increasing the survivability of personnel and scarce resources (both weapon systems and platforms) **[1]**. The application of IM can also have an important economic and logistic impact on stockpiling, storage and transport.

There are several approaches for the development of insensitive munitions, but prominent among them is the use of explosive fillings with reduced sensitivity, but in which performance is not compromised. Several important design considerations for such low sensitive explosive formulations include improvement of mechanical properties, reduced signature, extended service life and reduced environment impact during manufacture **[2]**.

Insensitive munitions are those which reliably fulfill their performance, readiness and operational requirements on demand, but in which the violence of response to unplanned hazardous stimuli is restricted to an acceptable level .There are two general approaches to explosive formulations which satisfy IM requirements. The first is through the use of polymer bonded explosives (PBXs), in which the energetic sensitive component is dispersed in a rubbery matrix. The second is through the use of intrinsically insensitive energetic ingredients such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB).

Many research where also focused on another possible intrinsically insensitive energetic material is 3-nitro-1, 2, 4-triazol-5- one (NTO) **[3 - 7]**.

In this work different explosive formulations based on NTO, which is an extremely insensitive explosive were prepared by casting with Trinitrotoluene (TNT) or Polyurethane (PU) to avoid casting problems originating from the high melting point of NTO.

2. EXPERIMENTAL

2.1 Materials

All the materials used in this work and their specifications are shown in table (1)

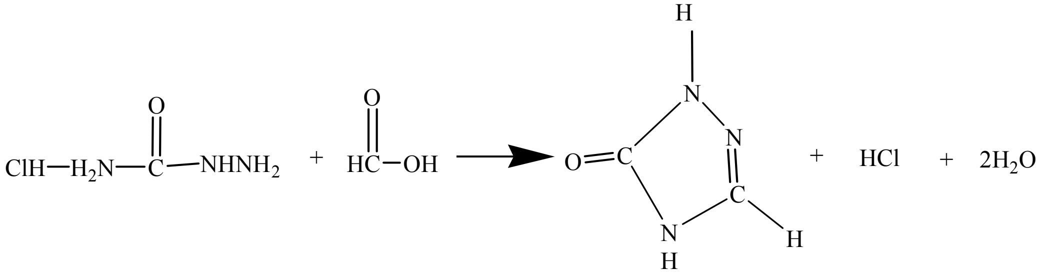
Table (1) Specifications of raw materials used in experimental work

Material	Purity (%)	Density (g/cm^3)	Boiling point (°C)	Source
Semicarbazide hydrochloride	98	-	173-178	SRL,India
Formic acid	85	1.20	101	Riedel-dehaen
Nitric acid	98	1.50		AZC,Egypt
HTPB	-	0.90	-	"Iverise co" Brazil
DOZ	-	0.91	376	Marano CO. Inc, New York, USA
HMDI	-	-	255	Aldrich, Germany
MAPO	-	1.1	159.5	Arsyn co Inc,USA

2.2 Preparation of NTO

2.2.1 Preparation of TO

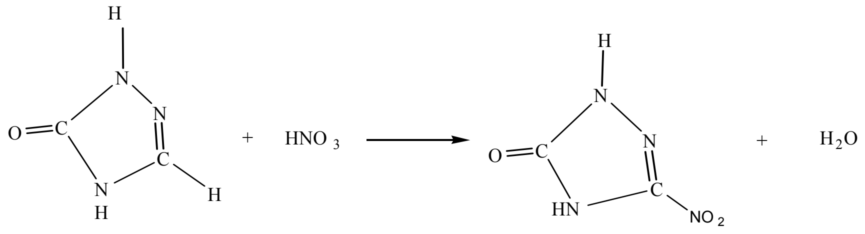
Formic acid was added proportionally to solid semicarbazide hydrochloride placed in three–necked round bottom nitrator. The mixture was magnetically stirred under reflux in temperature range 80-90 °C till dissolution of the entire solid semicarbazide hydrochloride. The excess formic acid was removed by normal distillation until the start of crystallization. Distilled water was added and distillation was continued till the start of the mixture dryness. Then mixture was cooled to room temperature overnight to be ready for nitration. Scheme 1 describes the chemical reaction equation of the formation of TO.



Scheme (1) Synthesis of TO

2.2.2 Nitration of TO

To a mechanically stirred nitrator, containing fuming nitric acid (98%), (TO) product was carefully added on fractions over a period of 120 minutes at 25 °C. The nitrated product was cooled down in a water bath then cold water was added to the nitrated mixture to precipitate NTO crystals. NTO crystals were purified by recrystallization from distilled water, filtered, washed with water and finally the product of NTO was dried at 60 °C for 24 hours. Scheme 2 describes the chemical reaction equation of the formation of NTO.



Scheme (2) Synthesis of NTO

2.3 Preparation of NTO-based explosives formulation

Based on the values of different explosive characteristics obtained by applying a novel computer program to calculate the explosive performance of different explosive formulations, the explosive mixtures (NTO/TNT 65:35, NTO/PU 88:12) were selected to be prepared experimentally and tested.

2.3.1 Preparation of NTO/TNT formulation using melt-casting technique

The calculated amount of TNT and NTO were accurately weighed. TNT was then placed into the glass flask (300 ml) and heated to 90 °C on a water bath for approximately 30 minutes. After complete melting of TNT, NTO was added slowly on stirring which was continued for approximately 30 minutes after complete addition of NTO to improve the mixing process. The molten mixture was then casted into suitable confinements to measure different explosive characteristics.

2.3.2 Preparation of NTO/PU PBXs using casting technique

The calculated amounts of HTPB as prepolymer, NTO and DOZ as plasticizer were accurately weighed. HTPB was then placed in a mixing kettle and mixed with two thirds of DOZ weight. NTO was then added in small portions during mixing for 1/2 hour. Thorough mixing was conducted for about 10 minutes after complete addition of NTO to ensure complete coating. The residual amount of DOZ, MAPO as bonding agent and HMDI as curing agent, calculated on basis of NCO/OH= 1.3, were added to the mixture and mixing continued for about 15 minutes. The formed matrix (paste) was then pressed into the mold relevant to each test. The prepared compositions were cured for 7 days at 55-60 °C.

2.4 Characterization of the prepared products

2.4.1 Melting point

Digital melting point apparatus, IA9000 – (UK), was used in measuring the melting point of TO and NTO.

2.4.2 Infrared Spectroscopy

Shimadzu 80000 series FTIR was used to identify the product through FTIR spectrum. The solid sample and KBr were ground, mix and press in the form of a disc having standard dimensions, The wave number range used was 500- 4000 cm^{-1} which represents the appropriate range for most organic compounds. Using the FTIR spectrum it was possible to identify the different functional groups in the prepared samples.

2.5 Sensitivity of different prepared explosive formulations

2.5.1 Determination of sensitivity to impact

Sensitivity to impact test was carried out using IKA-MASCHINENBAU apparatus by applying the standard test conditions **[8]**. The experiment was conducted using a weight of 5 kg and by changing the drop height. Six consecutive trials were performed for each drop height. The minimum height at which 100% initiation occurred was determined (the upper sensitivity limit); thus the energy required to initiate the explosive could be estimated.

2.5.2 Determination of sensitivity to friction

Chilworth BAM friction test apparatus, (UK), was used to determine the sensitivity to friction by applying the standard test conditions **[8]**. Sensitivity to friction was determined by spreading about 0.01g of the dry explosive on the surface of the porcelain plate in the form of a thin layer. Different loads were used to change the normal force between the porcelain pistil and the plate; force varied from nearly 5 to 360N.The sample initiation may be observed through sound, smoke appearance, or by the characteristic smell of the decomposition products. Six consecutive trials were performed for each load and lever position.

2.5.3 Determination of sensitivity to heat

(1) Ignition temperature

The ignition temperature was performed by using Chilworth deflagration test apparatus, made in UK, by employing the standard test conditions **[8]**.Three samples of 0.2 g each were dried up and ground to suitable particle size then inserted into 3 test tubes which were placed vertically into the heating block and the temperature was uniformly increased (5 °C/min) until deflagration of the sample occurred. The ignition temperature was read digitally on the control unit and the average temperature for the three samples was calculated.

(2) Ignition temperature at constant delay period of ignition (5 s)

Delay period of ignition of an explosive at certain temperature was experimentally determined by placing an explosive sample of a fixed mass at that temperature which should be higher than the previously determined ignition temperature of the explosive. The test is done using the same apparatus as before. The temperature was adjusted and fixed until the ignition took place and delay time was recorded. The samples of 0.05 g each were inserted into three test tubes already heated in the aluminum block to the investigated temperature and stopwatch was used to measure the time elapsed till ignition. The test was repeated at different temperatures till the obtained delay period was exactly 5±0.1 s.

3. RESULTS AND DISCUSSION

3.1 Results of Thermo chemical calculations for NTO based explosive formulations

The characteristics of explosive formulations are very important for theory and practice, because they allow evaluation and comparison of explosives and are necessary to determine the explosive composition which gives the required high performance. Besides the composition of products of explosive conversion there are also the specific volumes of products, explosion heat, and explosion temperature, power of explosive and explosive pressure. Knowing the composition of products of explosive conversion we may deal with calculating the other characteristics of explosives. The explosive characteristics of NTO and various formulations of NTO-TNT and NTO-PU calculated by using thermodynamic program are shown in table (2) and table (3).

It is obvious that for the formulations containing mixtures of NTO and TNT, explosion heat and temperature decrease as the weight percentage of NTO increase. On the other hand the values of the volume of detonation gaseous products, pressure, explosive force, and detonation velocity increase. This means that the shattering effect of the formulation (NTO/TNT) increases with increased NTO content.

For the formulations based on NTO/PU mixture, it is obvious that all parameters decrease with the weight percentage of PU increase. This means that the shattering effect of the formulation (NTO/PU) decreases with increased PU content.

Theoretical calculations obtained from the computer program showed that increase of NTO% in both prepared formulations (NTO/TNT) and (NTO/PU) causes an increase in the shattering effect and detonation velocity. We chose NTO/TNT (65/35) and NTO/PU (88/12) because of the process of casting ;(formulations higher than that percentage is difficult to cast).

Table (2) Explosive characteristics of NTO-TNT explosive formulations

Name		TNT pure	20%NTO 80%TNT	35%NTO 65%TNT	50%NTO 50%TNT	65%NTO 35%TNT	80%NTO 20%TNT	NTO pure
Summary formula	**C**	30.819	27.731	25.415	23.10	20.78	18.468	15.38
	H	22.013	20.686	19.691	18.697	17.7	16.707	15.38
	O	26.416	25.748	25.247	24.747	24.62	23.745	23.077
	N	13.208	16.720	19.355	21.984	24.24	27.258	30.77
ΔU_f (kcal/kg)		-27	-43.6	-56	-68.5	-80.95	-93.4	-110
ρ (g/cm^3)		1.65	1.7	1.738	1.775	1.812	1.87	1.9
Ob		-73.97	-64.09	-56.7	-49.3	-41.3	-34.5	-24.6
Gaseous product	**CO**	13.512	13.953	14.293	14.63	15.10	15.33	12.542
	CO_2	2.957	2.7515	2.594	2.43	2.35	2.10	2.83
	H_2O	6.99	6.289	5.767	5.25	4.82	4.22	4.87
	H_2	4.016	4.057	4.079	4.10	4.03	4.13	2.82
	N_2	6.604	8.36	9.678	10.99	12.12	13.63	15.325
	C	14.35	11.023	8.528	6.03	3.33	1.04	zero
$\sum n$ (moles)		34.079	35.41	36.41	37.4	38.4	39.4	38.5
V_O (cm^3/g)		763.37	793	815.58	838	861	883	861
D (m/s)		6913	7125	7279	7425	7604	7769.9	7891
P (kbar)		197.139	218	230	245	262	282	296
Q (kcal/kg)		1014	949	901	853	820	756	771
F (j/g)		967	982	992	999	1020	1004	1011
T (K)		3414	3338	3277	3211	3193	3064	3161

Table (3) Explosive characteristics of NTO-PU, PBXs formulations

Name		**90%NTO 10%PU**	**88%NTO 12%PU**	**85%NTO 15%PU**	**80%NTO 20%PU**	**NTO pure**
Summary formula	**C**	20.92	22.028	23.69	26.46	15.38
	H	24.49	26.31	29.05	33.60	15.38
	O	20.99	20.57	19.94	18.89	23.077
	N	27.75	27.15	26.24	24.74	30.77
ΔU_f (kcal/kg)		-112.8	-113.36	-114.2	-115.6	-110
ρ (g/cm^3)		1.82	1.8	1.78	1.74	1.9
Ob		-52.95	-58.625	-67.144	-81.328	-24.6
Gaseous product	**CO**	12.0386	11.293	10.179	8.345	12.542
	CO_2	1.611	1.553	1.459	1.2836	2.83
	H_2O	5.728	6.170	6.843	7.977	4.87
	H_2	6.561	6.984	7.682	7.682	2.82
	N_2	13.875	13.575	13.575	12.37	15.325
	C	7.27	9.181	12.052	16.831	zero
∑n (moles)		39.769	39.576	39.283	38.799	38.5
V_O (cm^3/g)		890.845	886.507	879.94	869.0957	861
D (m/s)		7244.662	7115.275	6960.959	6691.829	7891
P (kbar)		238.807	227.822	215.6245	194.795	296
Q (kcal/kg)		689.459	688.937	688.16	686.56	771
F (j/g)		860.522	837.311	804.9164	756.53	1011
T (K)		2602.54	2544.759	2464.539	2345.301	3161

3.2 Melting point

The melting point was measured for pure NTO and TO and found to be 263.5 °C , and 243 °C respectively. In the literature **[9],** the melting point of NTO and TO were found to be very close to the obtained experimental values(264 °C, and 244 °C respectively) which emphasize the purity of the obtained products.

3.3 Infrared spectroscopy

It is well known that the IR spectra of the organic compounds can be divided into three general regions, the functional region 4000 – 1300 cm $^{-1}$. The finger print region 1300 – 910 cm $^{-1}$ and the aromatic region from 910 – 500 cm $^{-1}$.The results obtained from the IR spectrum of TO and NTO are tabulated in table (4, 5) and the obtained absorption spectra for prepared TO and NTO are illustrated in figure (1) and figure (2) respectively

Table (4) IR characteristic absorption of TO

Group	**Wave number (cm^{-1})**	**Reference [10] (cm^{-1})**
N-H	3089.8	3300-2500
C-H	1255.6	1300-1000
C=O	1678	1850-1650
The ring	1020	1040-980
C=N	1699.2	1700-1600

Table (5) IR characteristic absorption of NTO

Group	Wave number (cm^{-1})	Reference [10] (cm^{-1})	NTO[11]
N-H	3209.3	3300-2500	3211
NO_2	1546.8	1550-1370	1546
Ring	1018.3	1040-980	1018
C=O	1716.5	1850-1650	1719
C=N	1701.1	1700-1600	-
C-N	829.3	870	-

It is clear from figures 1 and 2 that the NO_2 group which was not present in figure 1 relevant to TO, is found now in figure 2, relevant to NTO, as absorption peak at 1547 cm^{-1} which emphasizes the nitration step of TO to NTO.

3.4 Determination of explosive sensitivity to heat

Sensitivity of the prepared (NTO-TNT 65:35) and (NTO-PU 88:12) explosive formulations to thermal impulses was examined by measuring the ignition temperature and the delay period of ignition at constant temperature (higher than measured ignition temperature).

3.4.1 Ignition temperature

The results of the values of ignition temperature obtained for pure TNT, NTO, NTO/TNT (65:35), (NTO/PU) (88:12) are listed in table (6) with some relevant literature values. From these results obtained it can be seen that the ignition temperature for PBXs based on NTO and PU, seems to be slightly less than that obtained for pure NTO, pure TNT or (NTO-TNT) explosive formulation. The ignition temperature of NTO/TNT (65:35) explosive formulation (271 °C) was markedly less than that of pure TNT but very close to that of pure NTO. The found literature values for the ignition temperature of pure TNT and pure NTO are very close to those determined experimentally.

Table (6) Ignition temperature for NTO, TNT and (NTO/TNT, NTO/PU) formulations

Property	**Ignition temperature (^{0}C)**	**Literature**
NTO	274	280 **[1]** 266 **[9]**
TNT	300	300 **[12]**
NTO/TNT (65:35)	271	-
NTO/PU (88:12)	267	-

It is clear from table(6) that the ignition temperature for formulation (NTO/PU) 88:12 decreased with respect to pure NTO by 3% ,which can be attributed to the presence of a thin polymeric coat of the NTO crystals, which act as an energy barrier. It is clear from table (6) that the ignition temperature for formulation (NTO/TNT) 65:35 decreased with respect to pure NTO by 1%.

3.4.2 Ignition temperature at constant delay periods of ignition

The values obtained for the ignition temperature at constant delay periods of ignition (5 s) are tabulated in table (7)

Table (7) ignition temperature at constant delay periods of ignition of NTO, TNT, NTO/TNT (65/35), NTO/PU (88/12)

Property	**NTO**	**TNT**	**NTO/TNT**	**NTO/PU**
Ignition temperature at constant delay periods 5 s (^{0}C)	320	410	380	390

It is clear from table(7) that the delay period of ignition for formulation (NTO/PU) 88:12 increased with respect to pure NTO by 22% ,which can be attributed to the presence of a thin polymeric coat of the NTO crystals, which act as an energy barrier. It is clear from table (7) that the delay period of ignition for formulation (NTO/TNT) 65:35 increased with respect to pure NTO by 18%.

3.5 Sensitivity to impact

The results obtained for upper limit of sensitivity to impact energy are listed in table (8).It is clear that formulations based on polyurethane have lower sensitivity to impact than all other formulations based on TNT, or pure TNT and NTO due to the coating of the explosive grains by the polyurethane elastomer. The sensitivity to impact of (NTO -TNT) explosives formulation was markedly decreased when compared with that of pure TNT but higher than that of pure NTO.

Table (8) Sensitivity to impact for pure NTO, pure TNT, NTO/TNT (65/35) and NTO/PU (88/12)

Property	Impact energy [J] at 100 % initiation	Literature
NTO	30	22[13]
TNT	15	15[12]
NTO/TNT(65:35)	24	-
NTO/PU(88:12)	36	-

It is clear from table(8) that with respect to sensitivity of pure NTO to impact the formulation (NTO/PU) 88:12 sensitivity to impact was decreased by 20%,this can be attributed to the presence of a thin polymeric coat of the NTO crystals, which act as an energy barrier.

It is clear from table(8) that with respect to sensitivity of pure NTO to impact the formulation (NTO/TNT) 65:35 sensitivity to impact was increased by 20%

3.6 Sensitivity to friction

The results are tabulated in table (9); no indication of initiation was noticed even when applying the maximum force (360 N) of the test apparatus. Similar results were reported [14]. This high resistance to friction enables us to use these formulations in difficult (severe) conditions during production and handling.

Table (9) Sensitivity to friction for pure NTO, pure TNT, NTO/TNT (65/35) and NTO/PU (88/12)

Property	Friction force [N]	Literature
NTO	›360	>353[1]
TNT	›360	>353[1]
NTO/TNT(65:35)	›360	-
NTO/PU(88:12)	›360	-

It is clear from table (9) that the upper friction sensitivity limit could not be determined, and the formulation (NTO/PU) and (NTO/TNT) proved to be low sensitive to friction.

4. CONCLUSIONS

The experimental work showed that the NTO was successfully prepared in laboratory via the reaction of semicarbazide hydrochloride with formic acid to produce TO followed by its nitration with fuming nitric acid at 25 °C for 120 minutes with about 65% conversion. Theoretical calculations obtained from the computer program showed that increase of NTO% in both prepared formulations (NTO/TNT) and (NTO/PU) causes an increase in the shattering effect and detonation velocity.

Sensitivity to impact was determined and it was found that formulations based on NTO/PU have lowest sensitivity to impact (36 joule) when compared with pure NTO, TNT, and NTO/TNT. Sensitivity to friction showed that no initiation was noticed even when applying the maximum force (360 N). The ignition temperature of NTO/TNT (65:35) explosive formulation was 271 °C and for (NTO/PU) (88:12) explosive formulation was 267 °C.

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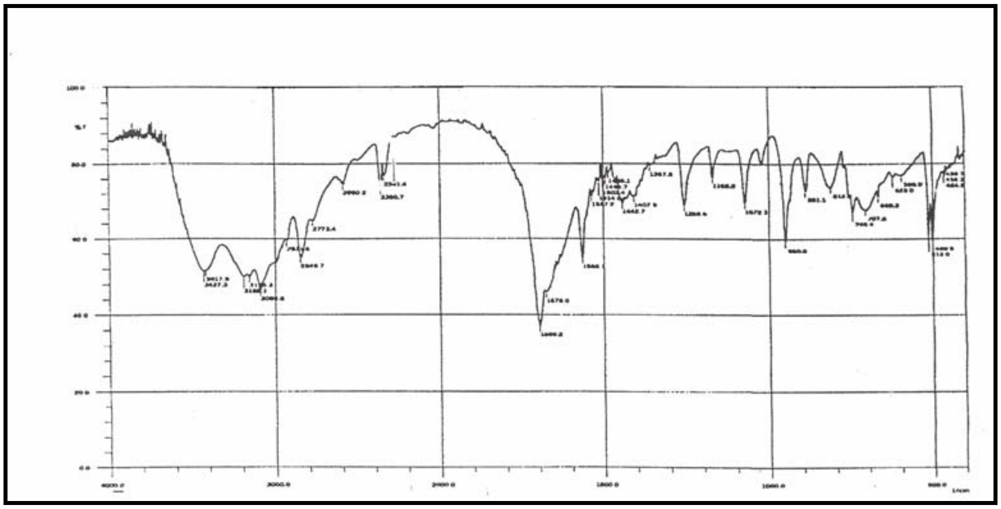

Fig (1) FTIR spectrum of prepared TO

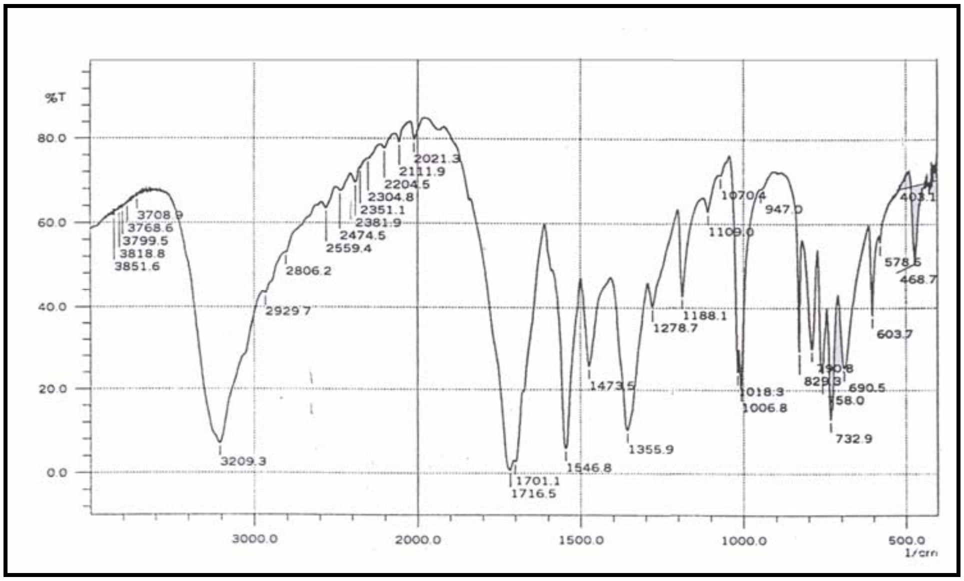

Fig (2) FTIR spectrum of prepared NTO