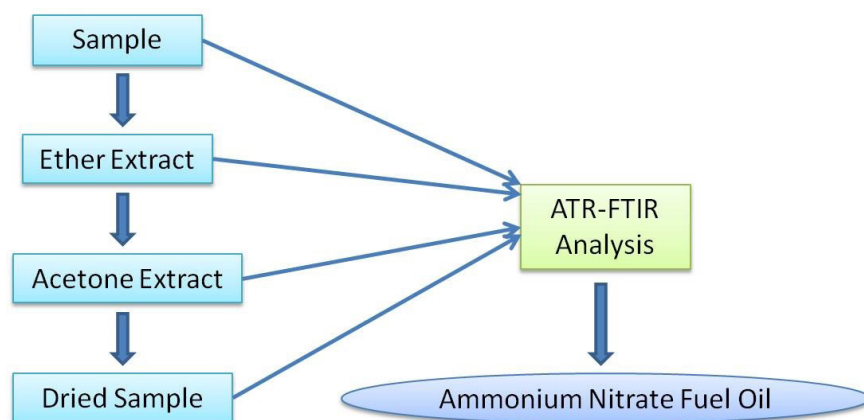**BrJAC**

Technical Note

Rapid Prediction of ANFO Based Explosives through ATR-FTIR Analysis – *Use of ATR-FTIR in Explosives*

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Ammonium Nitrate Fuel Oil (ANFO) is preferred mining explosives in worldwide. It is composed of ammonium nitrate (94-96%) and liquid hydrocarbon as fuel oil (4-6%), which is detonated through an explosive charge. In India, Forensic Science Laboratories received many criminal cases from investigation agencies for chemical analysis of sample as semi-solid materials supposed to be explosive material. In the present study, we developed an Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) procedure for easily analyzing the real crime exhibits related to ANFO based explosives. Firstly, semi-solid material is directly used on the ATR. Further, the sample is extracted using appropriate solvents (diethyl-ether/acetone). Extracts are subsequently analyzed on ATR-FTIR in comparison with standards for ammonium nitrate and diesel. The residue after acetone extract is dried and left solid material directly used on ATR for the detection of water-soluble compounds. The results significantly showed the presence of ammonium nitrate with the residue of diesel in a real crime exhibit. Hence, the proposed modify procedure can be advantageous for the rapid detection of diesel components mixed in ammonium nitrate through ATR-FTIR spectroscopy without the use of other chemical or instrumental analysis in a short period of time and also for easily identifying the presence of organic explosives (if any) among different samples received for the forensic opinion.

Keywords: Ammonium nitrate, ATR-FTIR, explosives, forensic analysis, fuel oil

INTRODUCTION

Ammonium nitrate (AN) is an extensively used chemical compound with numerous important applications. It is a crystalline powder varying in color from almost white to brown.[1] It is made by the reaction of ammonia (NH_3) with nitric acid (HNO_3) in water (H_2O) followed by careful evaporation of the

water to give up a solid material. It is a popular fertilizer because nitrogen is a key component of the two ingredients of the compound, i.e., ammonium (NH_4^+) and nitrate (NO_3^-). Ammonium nitrate as such does not ignite; but in contact with other flammable materials, it boosts fire risk and also supports fire even in the absence of oxygen. When involved in a fire, will stimulate burning and be classified as an oxidizer.[2] It is one of the main components in several types of mining explosives. It is combined with fuel oil and detonated through an explosive charge, where it is called an Ammonium Nitrate Fuel Oil (ANFO)-based explosive. ANFO is used as an explosive for mining, quarrying and civil construction purposes. As the constituents of ANFO are comparatively trouble-free to find, there is a potential for their improper use in improvised explosive devices (IEDs).[3]

ANFO is composed of around 94 to 96% ammonium nitrate and 4 to 6% fuel oil by weight. Ammonium nitrate (NH_4NO_3) is a strong oxidizing agent; and fuel oils are used for supply of fuel in preparation of ANFO-based compositions.[4] The fuel diesel, gasoline and sometimes kerosene are typically used in ANFO explosives, which can also be used as an indicator for fuel source recognition in explosive cases.[5] As ANFO consist of inorganic and organic ingredients, So the analysis of ingredients from ANFO based material has been classified into the determination of ammonium nitrate (inorganic part) and fuel oils (organic part) constituents. ANFOs are most widely used explosives all over the world.[4] During the last decades, ammonium nitrate has been involved in many industrial blasts, including the Beirut explosion in 2020 that killed 220 people and injured more than 6,500 instantly, Texas fertilizer plant explosion in 2013 that killed 15 people, a North Korean railway blast in 2004 that left 161 dead, and the 1995 Oklahoma City Bombing that left 168 souls lost, including 19 children, with several hundred more injured.[6] The most well-known incidents includes the explosion of an ammonium sulfate nitrate silo in Oppau (Germany) killed 507 and injured 1917 people in 1921.[7] 2000 suffered injuries in Texas serial plast due to ammonium nitrate during 1947,[8] and in 1994, the Asociación Mutual Israelita Argentina (AMIA) Jewish community center in Buenos Aires was bombed with the same chemical, killing 87 people.[9] At present, ANFO-based explosive materials account for most of the explosions that occurred in India, for example, the civil hospital blasts in Ahmedabad in 2008 and Mumbai in 2011.[10-11] In country like India, ANFO explosives are apparently found as ready mixed in a well packed plastic bag in the suspect's house during police patrolling and sometimes found as an undetonated product at the place of occurrence in the majority of criminal cases in the state of Madhya Pradesh. Investigation agencies usually send this suspected semi-solid material in plastic bags or plastic containers stated to be explosive material for the confirmation of chemical components to Forensic Science Laboratories.

Thus, the analysis of ingredients from any suspected explosives material is an important task for forensic chemists to recognize the type of explosive based on ingredients and ultimately support the investigation agency in exposing the connection to their probable root and origin. Many techniques have been usually employed for the identification of ANFO based preparations and their post blast residues. For example, Ion Chromatography (IC) was effectively able to detect ammonia and nitrate ions; presence of heavier hydrocarbons of fuel oil detected through Gas Chromatography–Mass Spectrometry (GC–MS).[12-13] Confocal Raman Spectroscopy was used to analyze the mixtures of ammonium nitrate (75% concentration) that may be found in real crime case samples of explosive threats.[14] Previously, Isotope Ratio Mass Spectrometry (IR-MS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) were evaluated for the discrimination of various forms of ammonium nitrate and its precursors to generate characteristic isotopic and elemental profiles.[15-16] However, the most fascinating area in the field of analytical chemistry is the use of non-destructive and eco-friendly techniques.[17] Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) has opened the window of opportunity for the identification and detection of bulk chemical components of crime exhibits in many forensic laboratories.[16] The ATR-FTIR could be used as a complementary and fast procedure for the analysis of post-blast residue in consumer fireworks.[18] The main benefits of the ATR method include a nominal or no requirement for sample preparation and its provision for high lateral spatial resolution. Suppajariyawat et al. reported the analysis of synthesized ANFO samples using GC-MS and ATR-FTIR.[19] However, the use of these techniques on real time samples

received by Forensic Science Laboratories has not been published. In the present study, an attempt has been made to develop an appropriate modified procedure for forensic researchers and explore the important role of the non-destructive ATR-FTIR technique in the analysis of real crime samples received in Forensic Science Laboratories for ANFO/Organic explosive ingredients. This study also highlighted the recovery of solid ammonium nitrate from real crime sample of ammonium nitrate fuel oil-based explosives using minimal use of organic solvents, which made this modified procedure as an eco-friendly technique in forensic chemistry.

MATERIALS AND METHODS

Diethyl ether (HPLC & Spectroscopy Grade, Purity 99.5%, CASR 60-29-7) and acetone (GC Grade, Purity 99.90%, CASR 67-64-1) were purchased from Finar Limited, Ahmedabad Gujrat, India. Iso-propyl alcohol (Purity 99%, CAS No. 67-63-0) was purchased from Loba Chemie Pvt. Ltd., Palghar, Maharashtra India. Whatman filter papers (No. 42, Ashless, Diameter 125 mm) was purchased from the authorized local vendor. The deionized water having Resistivity > 10 MΩ.cm was produced using Ion Exchange Lab Q Water System (ION EXCHANGE INDIA LTD. Mumbai, India) and used during chemical analysis.

Samples were seized by the investigating agencies as suspected explosive material. It was deposited for chemical identification of any "Explosive Substance" composition or any residue of explosive material. Figure 1 shows a schematic representation of the procedure for the analysis of a suspected explosive/ ANFO sample.
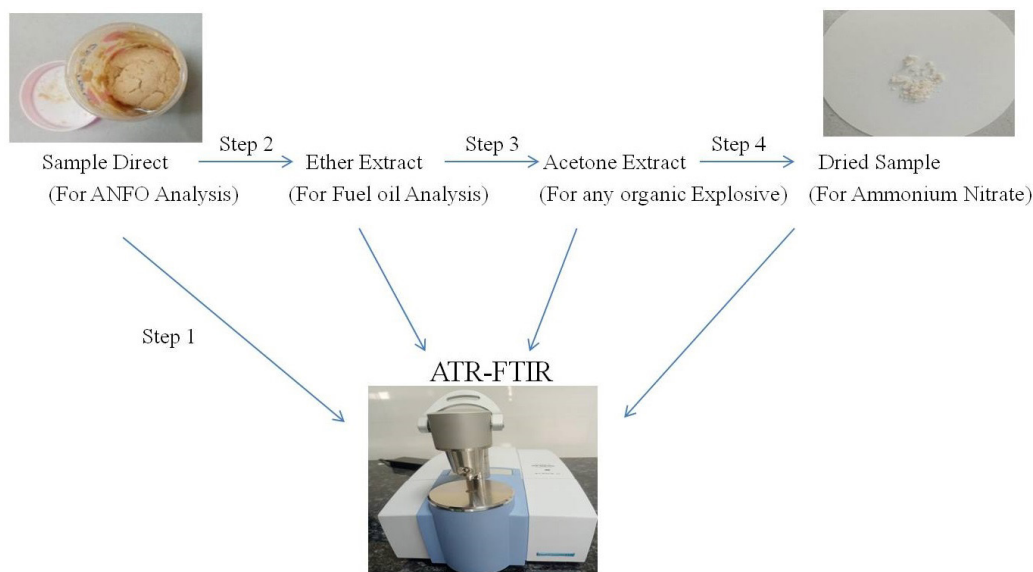

Figure 1. Schematic diagram of the procedure used for sample analysis.

Sample preparation/extraction procedure
Direct sample analysis

Some creamish coloured semi-solid sample suspected to be ANFO is directly applied and analyzed on the ATR-FTIR without any solvent treatment.

Diethyl-ether extraction

Some amount (approximately 1 g) of a creamish coloured semi-solid sample suspected to be ANFO is taken in test tube and extracted with diethyl-ether for fuel oil analysis. Briefly, 1 gram of sample and 2 ml of diethyl-ether are properly mixed using vortex. The diethyl-ether layer is poured from the test tube in a glass vial and concentrated to 20 µl. 10 µl of extract is taken and analyzed using a micropipette on ATR-FTIR for fuel oil analysis.

Acetone extraction

After extraction of diethyl-ether, residue of sample in test tube is further extracted with solvent acetone for the analysis of organic explosives. The acetone layer is poured from the test tube in a glass vial and concentrated to 20 µl. 10 µl of extract is taken and analyzed using a micropipette on ATR-FTIR for organic explosives analysis (if any).

Solid ammonium nitrate recovery procedure

After acetone extract preparation, acetone is evaporated from the residue of sample and the sample is dried at room temperature, resulting in the formation of powdery material. Finally, powdery material is directly analyzed on the ATR diamond for ammonium nitrate recovery.

ATR-FTIR analysis

Infrared (IR) spectra are recorded on a Bruker ALPHA II FT-IR spectrometer (Brucker Optick GmbH, Ettlingen, Germany) equipped with a Single-reflectance diamond ATR accessory exhibiting a Single-reflectance (45°) diamond crystal (Bruker Platinum ATR) with an approximately 0.6 mm × 0.6 mm active area and a deuterated triglycine sulfate (DTGS) detector. IR absorption spectra are recorded from 4000 to 400 cm^{-1} using a spectral resolution of 4. Before each measurement, the crystal is carefully cleaned with isopropanol, and a background spectrum is recorded. For each real sample analysis, samples are dropped over the dry surface of the ATR prism. Five replicated spectra are recorded to assess precision and ensure the reproducibility of each sample. For every measurement, the system performed twenty-three scans, which are automatically averaged using the Opus 8.7.31 software in order to obtain spectra with a good signal-to-noise ratio. The ATR prism is cleaned and tested regularly between the measurements, and an absorption spectrum is recorded without the sample to ensure that it has no peaks above the regular environmental noise level. The laboratory conditions of relative humidity and temperature during the analysis are kept around $39 \pm 8.0\%$ and 23.7 ± 2.0 °C, respectively.

RESULTS AND DISCUSSION

Functional groups in the ingredients of chemical substances could be easily examined by the characteristic absorption band pattern of each group of atoms in the FT-IR spectra.[11] ATR-FTIR spectra of ammonium nitrate standard crystals are presented in Figure 2.
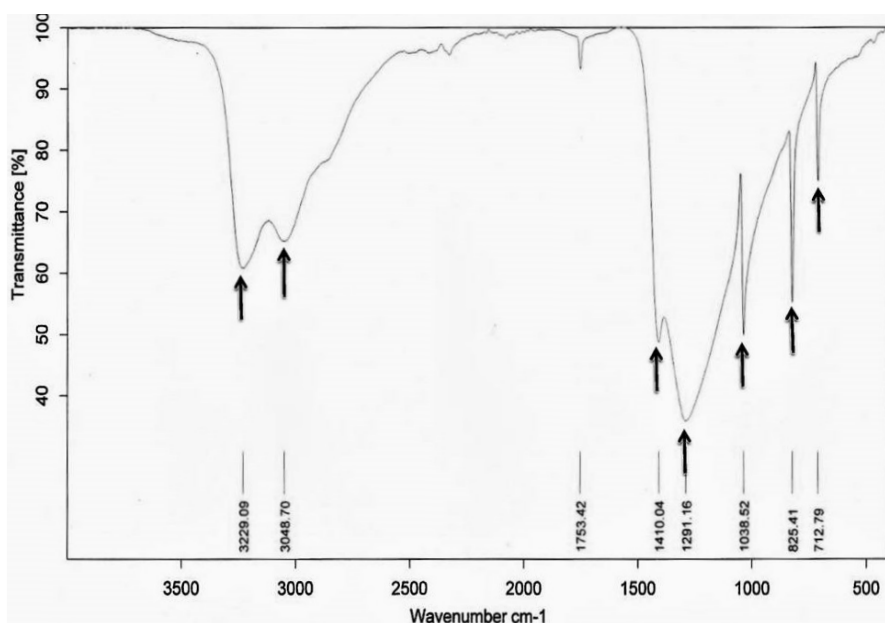

Figure 2. FTIR spectra of ammonium nitrate.

In general, ammonium nitrate spectra show two main characteristic signals of NH_4^+ ions and NO_3^- ions. The NH_4^+ ions have consistently 2 characteristic bands; i.e., a very strong broad band at 3020 to 3330 cm^{-1} and a strong absorption region at 1325 to 1480 cm^{-1}. It has no bands developing below 714 cm^{-1}. The NO_3^- ions have a very strong broad absorption band at 1280–1520 cm^{-1}, three weak bands in the region of 700–740 cm^{-1}, 1020–1070 cm^{-1} and 1720–1800 cm^{-1}, and a sharp, less intense band also observed at 840–800 cm^{-1}. These signals are the major characteristic of the ammonium nitrate compound in ATR-FTIR, which confirmed the vibrational mode of both ions.[13] The spectrum show two peaks labelled at 3048 cm^{-1} and 3225 cm^{-1}, could be related to the vibrational frequencies of NH_4^+ ions. The strong vibrational frequencies of NO_3^- ions peaks have labelled at 1291 cm^{-1} and 1409 cm^{-1}. The bands appearing at 713 cm^{-1}, 826 cm^{-1}, 1040 cm^{-1} and 1753 cm^{-1} have resulted from weak vibrational frequencies of NO_3^- ions.

The diesel sample from the local area is taken for analysis, and a spectrum is shown in Figure 3. As aliphatic hydrocarbons (paraffin) are the main components of diesel fuel, they mostly express the vibrational features of an aliphatic C-H stretching in the region at 2800–3200 cm^{-1} and the C-H deformation at around 1350–1470 cm^{-1}.[14] IR spectra of the diesel sample have confirmed the presence of three characteristic peaks of diesel, labelled at 2853 cm^{-1}, 2921 cm^{-1} and 2954 cm^{-1} which are related to the vibrational aliphatic C-H group stretching. The peaks observed and labelled at 1377 cm^{-1} and 1459 cm^{-1} resulted from the absorption band of C-H group deformation.
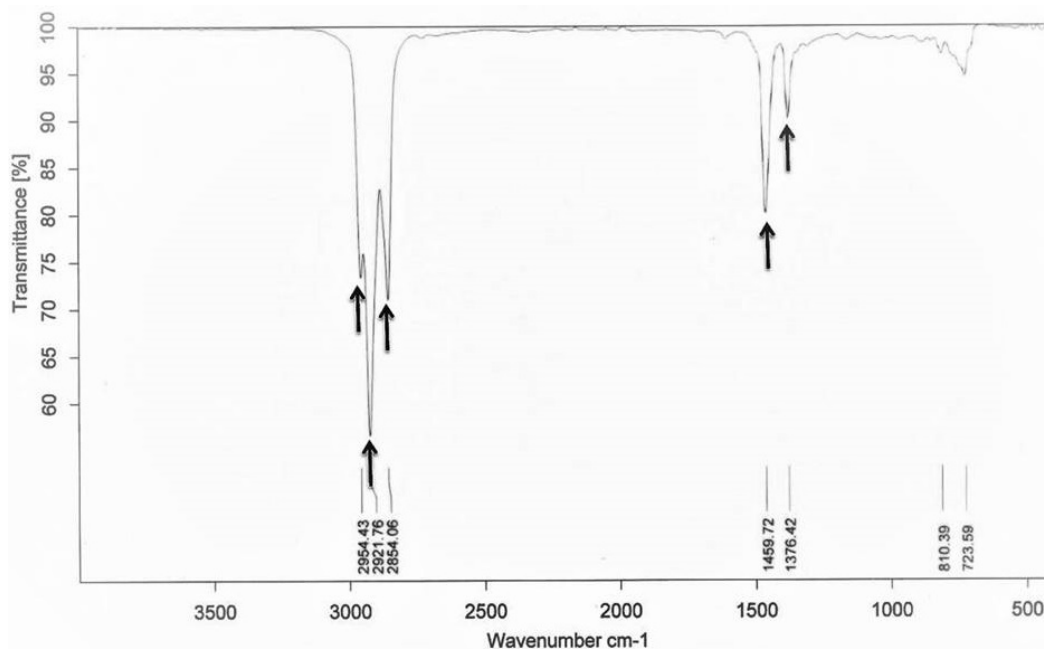

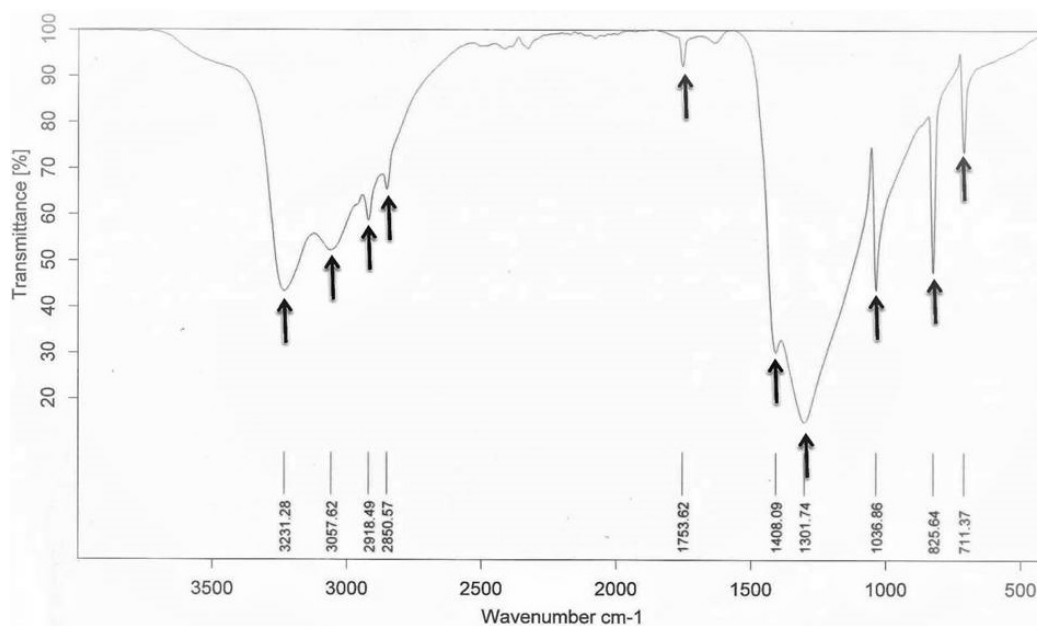**Figure 3.** FTIR spectra of diesel.

Figure 4. FTIR spectra of semi-solid sample.

Firstly, the semi-solid sample stated to be explosive was directly analyzed on ATR-FTIR and presented in Figure 4. The sample has shown spectra that are slight similar to those of ammonium nitrate spectra along with characteristic peaks of N–H stretching vibration in the region 3020 to 3330 cm^{-1} and N-O stretching and NO group deformation in the regions of 700–770 cm^{-1}, 800–860 cm^{-1}, 1015–1070 cm^{-1}, 1280–1520 cm^{-1} and 1700–1800 cm^{-1}. The FTIR spectrum of ammonium nitrate produced strong signals resulting from NO_2 group asymmetric stretches in the range 1325–1425 cm^{-1} and NO group deformations in the region 860–800 cm^{-1}. These signals from a semi-solid sample in IR could be the main aspect of the ammonium nitrate compound. But the FTIR spectra of the tested sample did not visually display any significant differences when compared to the standard spectrum of ammonium nitrate. Also, the main FTIR signals of diesel standard, including C-H deformation and C-H stretches, are completely hidden under the ammonium nitrate spectrum of the semi-solid sample. This is expected because FTIR analysis does not usually present enough sensitivity to a low percentage of unknown substances, which could be buried in the suspected sample as explosive material.[19] As FTIR did not evidently distinguish different peaks specifying the components of ANFO, it is difficult to say that a suspected explosive compound is ANFO or not; because it is uncertain whether ammonium nitrate is present in the form of a pure substance or blended with any fuel oil. It is necessary to extract the fuel oil component from the matrix. So, the sample is extracted using a suitable solvent, i.e., diethyl-ether to extract out the fuel oil part of the sample. The FTIR spectrum of concentrated organic extract is characterized by ATR-FTIR and is presented in Figure 5.

The maximum intensive bands are caused by C–H groups stretching in the region between 3000–2800 cm^{-1} and angular deformations at 1461 cm^{-1} and 1383 cm^{-1}; which confirmed the presence of characteristic peaks of diesel residue in semi-solid sample, as previously shown in Figure 3. Other peaks could corroborate the presence of aromatic compounds along with components of biodiesel. Aromatic compounds showed characteristic bands of low intensity in the region 900–675 cm^{-1} from the C–H out of line angular deformation. Nespeca et al reported that biodiesel in diethyl-ether extract is observed by the carbonyl absorption band near 1750–1735 cm^{-1}.[20] As a good practice, it is essential to screen the sample for high explosive residues during forensic examination. So, after the fuel oil analysis, acetone extract is prepared for screening of high explosive residues. However, it is also of greater importance in handling the ANFO-like material in the laboratory during analysis. Scientists should ensure that such type of compund is not exposed to strong shock waves from other explosives and also avoid contamination with combustible materials or organic substances and inorganic materials that may contribute to its sensitivity to explosion.[21]
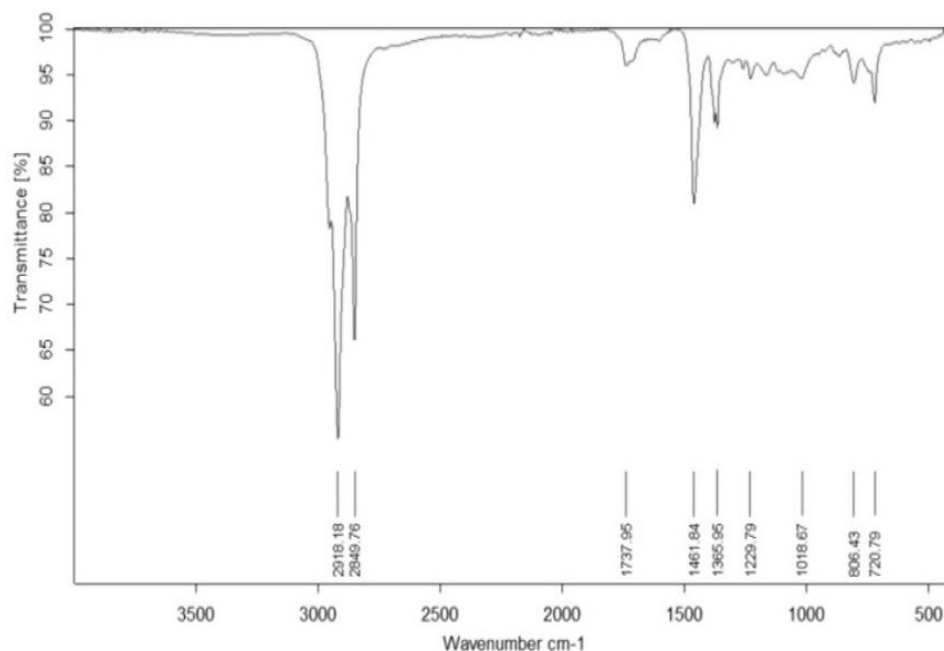
Figure 5. FTIR spectra of diethyl-ether extract from sample.

Acetone extract is dried on aluminium foil and then analyzed on an ATR diamond. No high explosive residue was detected in the acetone extract of the sample (data not presented). Finally, a powdery material is prepared after the evaporation of acetone from the sample. Powdery material is directly analyzed on the ATR-FTIR and spectra are presented in Figure 6.
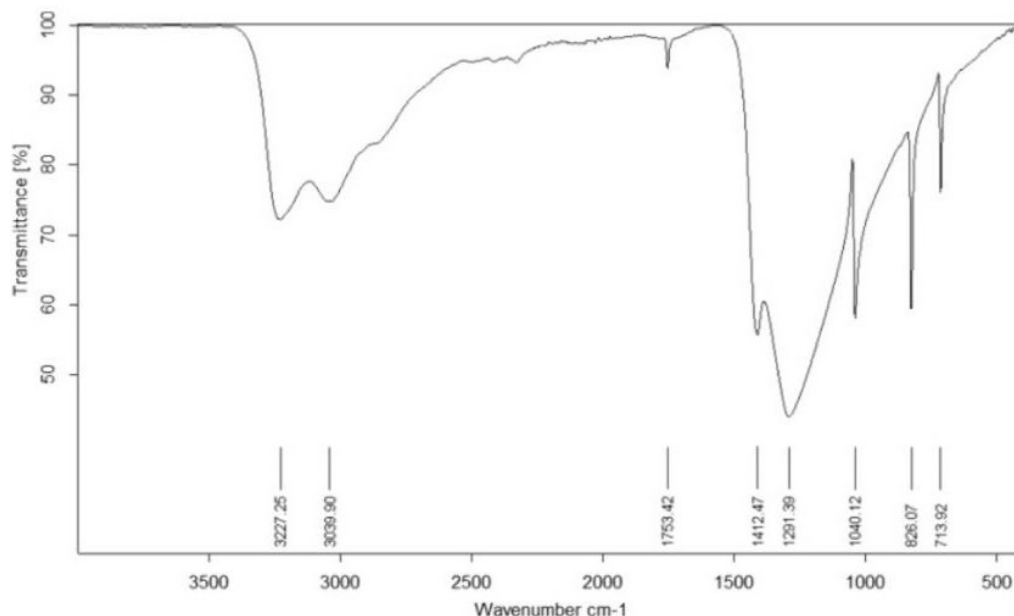

Figure 6. FTIR spectra of powdery material obtained after extract.

Two characteristic bands (as mentioned previously in Figure 2) of ammonium nitrate can be easily identified in the powdery sample, which confirmed the presence of characteristic peaks of ammonium nitrate in the extract from the sample. The spectra of semi-solid material do not give a clear conclusion

about the presence of ammonium nitrate and fuel oil components in the sample, as ammonium nitrate dominates in the spectra. But after following the procedure as mentioned in Figure.1, spectra of ether extract closely match with the diesel standard. Similarly, the spectra of powdery material after acetone extract are matched with the ammonium nitrate standard. ANFO is cheaper than other high explosives such as Trinitrotoluene (TNT), Cyclonite (RDX), Pentaerythritol tetranitrate (PETN), Nitroglycerin (NG) etc. Its easy availability and easy preparation as improvised explosive devices which made it more popular with blasting agencies, anti-social elements and terrorists.[4] So, analysis of this type of sample should be carried out by the forensic laboratories in India. Hence, the proposed procedure can be advantageous in forensic investigation for easy and fast detection of suspected ANFO samples.

CONCLUSIONS

ANFO is the most popular industrial explosive and is used as an oxidizing agent. It is also used as the main charge in improvised explosive devices by the group of terrorists due to its high stability and easy availability. In various states of India, like West Bengal and Madhya Pradesh, most of the blasting incidents has been reported due to this low-cost explosive. This work has aimed to develop a simple, accurate, and fast analytical method of detection based on ATR-FTIR spectroscopy to determine the ingredients of ANFO in crime exhibits with minimal use of chemical solvents for forensic science laboratories. The present study proved that ATR-FTIR analysis can be one of the best choices to identify ANFO-based explosives from different crime scenes and arrange intelligence information by collecting the data for forensic research and analysis. Since the application of the ATR-FTIR methodology is capable of cutting down costs and boosting considerably the classification frequency; FTIR analysis also gains attention due to minimal sample preparation, minimal use of solvents and chemical reagents without generating any harmful waste. For this study to be useful, each forensic science laboratory could use this method of analysis for ANFO/Explosive samples and develop the same method to establish selective identification in criminal cases.

Conflicts of interest

The authors declare that they have no conflict of interest.

REFERENCES
(1) Rao, P. S. Ammonium Nitrate. In: Wexler, P. (Editor), *Encyclopedia of Toxicology* (Third Edition). Academic Press, 2014, pp 209-211. https://doi.org/10.1016/B978-0-12-386454-3.00235-9.
(2) Tenchov, R. Ammonium nitrate: making it safer today for a better tomorrow. *CAS Insights*, November 23, 2022. https://www.cas.org/fr/node/34356 (accessed 2023-11-07).
(3) Kulkarni, S. Explained: What is ammonium nitrate, which caused the Beirut explosion? *The Indian Express* (India), August 10, 2020. https://indianexpress.com/article/explained/explained-what-is-ammonium-nitrate-which-caused-the-massive-explosion-in-beirut-6540646/ (accessed 2023-11-07).
(4) Fabin, M.; Jarosz, T. Improving ANFO: Effect of Additives and Ammonium Nitrate Morphology on Detonation Parameters. *Materials* **2021**, *14* (19), 5745. https://doi.org/10.3390/ma14195745.
(5) Gonzalez-Rodriguez, J. Tracking the origin of fuel oil and petrol in explosive mixtures of ANFO. *Annals of Medicine* **2019**, *51* (sup 1), 30. https://doi.org/10.1080/07853890.2018.1560070.
(6) Substance that reportedly sparked Beirut explosions was used in the 1995 Oklahoma City bombing. *CBS News*, August 6, 2020. https://www.cbsnews.com/news/ammonium-nitrate-beirut-explosion/ (accessed 2023-11-07)

(7)   Hörcher, U. Oppau 1921: Old Facts Revisited. *Chemical Engineering Transactions* **2016**, *48*, 745-750. https://doi.org/10.3303/CET1648125.

(8)   Britannica, The Editors of Encyclopaedia. "Texas City explosion of 1947." *Encyclopedia Britannica*, September 22, 2023. https://www.britannica.com/event/Texas-City-explosion-of-1947. (accessed 2023-11-07).

(9)   Bard, M. Terrorism: Bombings in Argentina, March 17, 1992; July 18, 1994. *Jewish Virtual Library*. https://www.jewishvirtuallibrary.org/terrorist-bombings-in-argentina (accessed 2023-11-07).

(10)   Shastri, P. 22 kg ANFO was used in Civil Hospital blast. *The Times of India* (India), August 9, 2008, http://timesofindia.indiatimes.com/articleshow/3344355.cms?utm_source=contentofinterest&utm_medium=text&utm_campaign=cppst (accessed 2023-11-07).

(11)   Thaver, M. Ammonium nitrate, fuel oil was used. *Hindustan Times*, July 24, 2011. https://www.hindustantimes.com/mumbai/ammonium-nitrate-fuel-oil-was-used/story-qycQdGNncihhIdikn4BLjJ.html (accessed 2023-11-07).

(12)   Michalski, R.; Kurzyca, I. Determination of Nitrogen Species (Nitrate, Nitrite and Ammonia Ions) in Environmental Samples by Ion Chromatography. *Pol. J. Environ. Stud.* **2006**, *15* (1), 5-18.

(13)   Fernández-Varela, R.; Andrade, J. M.; Muniategui, S.; Prada, D.; Ramírez-Villalobos, F. The comparison of two heavy fuel oils in composition and weathering pattern, based on IR, GC-FID and GC–MS analyses: Application to the Prestige wreackage. *Water Res.* **2009**, *43* (4), 1015-1026.

(14)   Daniel, D.; David, W. H. Raman Spectroscopy for Detection of Ammonium Nitrate as an Explosive Precursor used in Improvised Explosive Devices. *Spectrochim. Acta, Part A* **2020**, *233*, 118204. https://doi.org/10.1016/j.saa.2020.118204.

(15)   Benson, S. J.; Lennard, C. J.; Maynard, P.; Hill, D. M.; Andrew, A. S.; Roux, C. Forensic analysis of explosives using isotope ratio mass spectrometry (IRMS)-preliminary study on TATP and PETN. *Sci. Justice* **2009**, *49* (2), 81-86. https://doi.org/10.1016/j.scijus.2009.03.004.

(16)   Joshua, A.; D'Uva, D. D.; Simon, W. L. Source determination of homemade ammonium nitrate using ATR-FTIR spectroscopy, trace elemental analysis and chemometrics. *Forensic Chem.* **2022**, *28*, 100411. https://doi.org/10.1016/j.forc.2022.100411.

(17)   Liu, G. L.; Kazarian, S. G. Recent advances and applications to cultural heritage using ATR-FTIR spectroscopy and ATR-FTIR spectroscopic imaging. *Analyst* **2022**, *147*, 1777-1797. https://doi.org/10.1039/d2an00005a.

(18)   Martín-Alberca, C.; Zapata, F.; Carrascosa, H.; Ortega-Ojeda, F. E.; García-Ruiz, C. Study of consumer fireworks post-blast residues by ATR-FTIR. *Talanta* **2016**, *149*, 257-265. https://doi.org/10.1016/j.talanta.2015.11.070.

(19)   Suppajariyawat, P.; Elie, M.; Baron, M.; Gonzalez-Rodriguez, J. Classification of ANFO samples based on their fuel composition by GC-MS and FTIR combined with chemometrics. *Forensic Sci. Int.* **2019**, *301*, 415-425. https://doi.org/10.1016/j.forsciint.2019.06.001.

(20)   Nespeca, M. G.; Hatanaka, R. R.; Flumignan, D.; de Oliveira, J. E. Rapid and Simultaneous Prediction of Eight Diesel Quality Parameters through ATR-FTIR Analysis. *J. Anal. Methods Chem.* **2018**, *2018*, 1795624. https://doi.org/10.1155/2018/1795624.

(21)   United States Environmental Protection Agency (EPA), National Service Center for Environmental Publications. *Chemical Advisory: Safe Storage, Handling, and Management of Solid Ammonium Nitrate Prills*, 2015. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100V369.txt (accessed 2023-11-07).