Forensic Instrumental Analysis of Post-Blast Inorganic Residues in Soils

D. Kumar[1], Prajakta Uday Kotawadekar [2], Richa Singh[3], Karishma Ranjan[3]

[1]Scientist-B (Explosives), Central Forensic Science Laboratory, Pune,
[2]Forensic Professional (Fact Plus), Central Forensic Science Laboratory, Pune,
[3]Forensic Professional (Fact), Central Forensic Science Laboratory, Pune,
[1,2,3]Directorate of Forensic Science Services, Ministry of Home Affairs, Government of India

Abstract

This work focuses on the trace analysis of nitrate ion (NO_3^-) content in post-blast explosion debris from pit soil samples and its control soil sample using Ion Chromatography (IC), an essential technique for inorganic explosives ion detection and confirmation. Blast simulations of pyrotechnics were conducted under a controlled environment in an agricultural land at Talegaon, Pune, India and a residential area at Nigadi, Pune, India. Explosion debris along with Pit Soil were collected from the pit of both sites. The control soil samples were collected from distance of 5 meters away from the explosion pits. A sensitive ion chromatographic method was used to detect the presence of nitrate ions in explosion debris and the control soil samples. The results provide insights into the interference caused by the common ions present both in explosion debris and the control soils. This study throws light on importance of testing of a control sample. The present study guides the forensic analyst in making correct interpretation of results based on comparative study of levels of nitrate ions in exhibits and its control.

Keywords: Pit Soil, Control Soil, Pyrotechnic, Nitrate ions, Ion Chromatography, Post-Blast Residues

1. Introduction

Explosion involves a rapid combustion reaction releasing large amount of energy. This energy in the form of heat, sound and shock waves propagate damage to the surroundings and life around the explosion site.[1] In case of bomb blasts, the criminal justice system asks whether the causative agent is indeed an explosive substance, only then can the culprits be charged with the penalties under the relevant statutory law. Hence, forensic analysis of exhibits in post-blast scenario involves conclusive determination of explosive nature of the substance and further, a definite confirmation of category and identity of such explosive substance. The forensic lab is required to perform various presumptive and confirmative tests on the exhibit samples in order to identify the explosive residue.[2] The explosive residue is unexploded portion of the original explosive composition remaining after the explosion has taken place. At a post blast bomb scene, these are the species that provide the invaluable clues as to the identity of the explosive material used for the bombing episode.[3]

Oxidisers and fuel are the major components of any explosive composition. Metal or ammonium-based nitrates, chlorates, perchlorates, permanganates, chromates, peroxides are common oxidising agents used along with fuels like sulphur, charcoal, other metals in case of in-organic low explosives mixtures. [4] Many cases involves perpetrators making use of Improvised explosive devices (IEDs) or simpler home-made explosives utilising low explosive mixtures. Ease of availability, low cost and legality of purchase of inorganic salts and peroxides make them lucrative resources for the home-made explosive devices used by perpetrators.[5],[6]. Urea nitrate and ammonium nitrate with fuel oils are basis of many home made explosive devices.[1] Nitrate and Nitrate + Chlorate based explosive compositions are found to be used in greatest proportion of the blasts in India. Potassium nitrate, a non-explosive substances as fertilizers not covered under statutory law are easily available and can be legally procured to perform illegal explosion activities.[4] The residues of inorganic low explosives are ionic species that pin-point towards the nature and source of the explosive material. Hence a forensic analyst needs a method which can identify these ionic species which further can help to deduce the type of inorganic residue. For example, the most common ionic residues in case of black powder based explosives are K^+, Na^+, NO_3^-, SO_4^{2-}, where as in case of ammonium nitrate are NO_3^- and NH_4^+.[6]

Experience of the authors says that forensic analysis of explosive residues from post-blast sites and interpretation of their results is not an easy task. The task is made difficult by the fact that explosion is itself a highly uncontrolled and heterogeneous phenomenon. The explosive residues along with the explosion debris get dispersed in the non-homogenous matrix like soil of the explosion site. The matrix effects of the exhibit influences the recovery of the inorganic residues from the debris.[6],[7] Obtaining a representative sample of trace levels of explosive residues from an explosion site which can span over a vast area doesn't make this task any easier. To further complicate the matters, in-organic explosive residues are quite ordinary ions which are found even in the non-explosive materials of daily use and environment like soil, debris and dust.[8] Usage of nitrate based fertilisers contributes to the availability of Nitrate ions as common interferers in samples of soils.

These ordinary ions are highly available, although in very low background levels. Detection and comparison of such low levels of interfering ions in the exhibit and its control sample, requires use of a highly selective and sensitive method which can distinguish the response of the interfering ions and that of the explosive ions.[9] The forensic labs use methods like spot test, TLC, FT-IR, Ion Chromatography, Capillary Electrophoresis, ED-XRF for analysis of inorganic explosives residues.[10] However, Ion Chromatography (IC) is considered to be the best suited method for analysis of inorganic ions at trace level due to its high selectivity, sensitivity, robustness, reliability and ease of use for both qualitative and quantitative purposes.[9]

Present study involves comparative analysis of the soil samples from explosion pits and the control soil sample collected at distance of 5 meters from two sites located at Talegaon and Nigadi in Pune,   India. The comparative study was done to detect the levels of nitrate ions in debris collected from the explosion pit and the control soil sample of the same site. The study focuses on analysis of Nitrate ions as nitrate based explosive mixtures are most common in bomb-blast cases and they are most common interferer ions found in the surroundings like soil, dust, debris. Detection of nitrate ions in the extracts of the exhibits indicate use of any nitrate salt based explosive composition for that explosion

phenomenon.[11] This study aims to identify difference if any in the ions concentration in the exhibits and its control sample and how the analyst must derive his opinion by careful interpretation of test results and findings.

2. Experimental Section

2.1. Materials and Methods

Pyrotechnic sample (fire-crackers) was obtained from local market in Pune district; Demineralised (DM) water procured from Labogen Fine Chem Industry, Ludhiana; Allpure Nylon Syringe filter (pore size 0.22 μm) was procured from Membrane Solutions ; and Filter paper procured from Clairofit (India), Bhiwandi.

For Ion Chromatography, Metrohm Advanced IC system by Metrohm Ltd (Herisau, Switzerland) fitted with Metrosep A Supp 19 anion exchange column and ANION Eco IC 1 Conductivity detector was used. Standard anions solutions of 10ppm, 5ppm and 1ppm were prepared from 10 ppm Standard Anion mix procured from Sigma Aldrich (Switzerland). The mobile phase for anion analysis was prepared using analytical grade sodium bicarbonate and sodium hydrogen carbonate from Merck (Germany), and Acetone from Advent Chembio Pvt. Ltd, Navi Mumbai. Analytical grade sulfuric acid solution obtained from Sigma Aldrich (Switzerland) was used for Suppressor solution.

2.2. Pyrotechnic blast simulation procedure

Blast simulations of pyrotechnics were conducted in a controlled condition on agricultural land at Talegaon, Pune and a residential area at Nigadi, Pune. Isolated sites were chosen to avoid disturbance and harm to the public and property. The sites contained soil to serve purposeful during sample collection and analysis.

2.3. Sample collection

For post-blast samples, the debris of the exploded pyrotechnic along with soil were collected from the explosion pit using a spatula and packed in a labelled self-sealing polythene packet. Control samples of soil were collected from around 5 metres away in a separate labelled self-sealing polythene packet. Same method was followed for both explosion simulation sites. An unexploded pyrotechnic was packed in a separate labelled self-sealing polythene packet.

2.4. Sample preparation

Unexploded pyrotechnic was dismantled using proper care and safety measure. The entire content of the dismantled pyrotechnic was taken in a beaker and labelled as 'PT'. 'Explosion debris along with pit soil' collected at Talegaon and Nigadi were labelled as 'ED-T' & 'ED-N' respectively and 'Control Soil' collected at Talegaon and Nigadi were labelled as 'CS-T' & 'CS-N' respectively. Equal quantity of 'ED-T', 'ED-N', 'CS-T' & 'CS-N' were taken in separate beakers.

For extraction of nitrate ions, 50ml each DM water was added to beakers containing samples 'ED-T', 'ED-N', 'CS-T' & 'CS-N' and 'PT' . The extracts were filtered using filter paper. The same procedure

was repeated twice with 50ml portion of DM water to recover nitrate ion completely. The collected filtrates were combined and evaporated to dryness. The extracts were reconstituted in 100mL DM water each. 10 mL portion of each was syringe filtered to remove any fine particulates. An aliquot of syringe filtered extract was injected on the IC Column for analysis.

2.5. Methodology used in Ion Chromatography

The IC system comprised of Methrohm 830 IC interface, ANION Eco IC 1 Conductivity detector, 820 column thermostat, 818 IC pump, separation column and Metrosep A SUPP 4/5 guard column. The column used for anionic separation was Metrosep A Supp 19, 150 x 4.0 mm with 4.6 μm particle size, and Hydrophilic polystyrene/divinylbenzene copolymer with quaternary ammonium groups as column packing material. The flow rate was set at 0.7 mL/min. The anionic eluent used was 8.0mM Na_2CO_3 + 0.25mM $NaHCO_3$ [12].

The ion chromatogram of the Blank (DM water), Standard Anion Mix , extracts of 'ED-T', 'ED-N', 'CS-T' & 'CS-N' and 'PT' samples were obtained by using the above IC method. Detection parameters such as Retention Time (RT), Area, Height and Concentration were noted. The retention time (RT) of nitrate ions peak in chromatogram of the Standard Anion Mix was used to identify the peak of nitrate ions in 'ED-T', 'ED-N', 'CS-T' & 'CS-N' and 'PT' samples. Linearity was obtained using the 10ppm, 5ppm & 1 ppm solutions of Standard Anion Mix. The said linearity was used to obtain the concentration of the nitrate ions in 'ED-T', 'ED-N', 'CS-T' & 'CS-N' and 'PT' samples.

3. Observation

The detection parameters (RT, Area and Height) of blank and 10ppm, 5ppm & 1 ppm solutions are given in table 1. The linearity obtained is depicted in fig.1.

The detection parameters of samples 'PT', 'CS-T', 'ED-T', 'CS-N' and 'ED-N' are given in table 2. The chromatograms of samples 'PT', 'CS-T', 'ED-T', 'CS-N' and 'ED-N' are given in Fig. 2 to Fig.6.

Table 1: Detection parameters of blank and standard anion mix

Sample ID	Retention time (min)	Area (μS/cm) x min
Blank	No peak observed	NA
1 ppm std	12.44	0.106
5 ppm std	12.42	0.507
10 ppm std	12.43	0.92

Figure 1: Standard curve of concentration against peak area
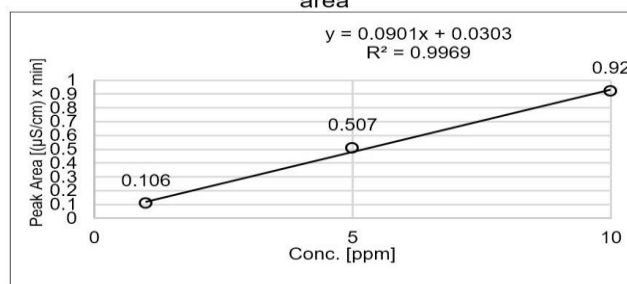
Table 2: Detection parameters of samples

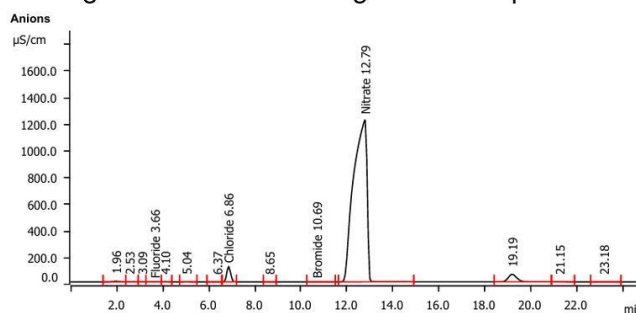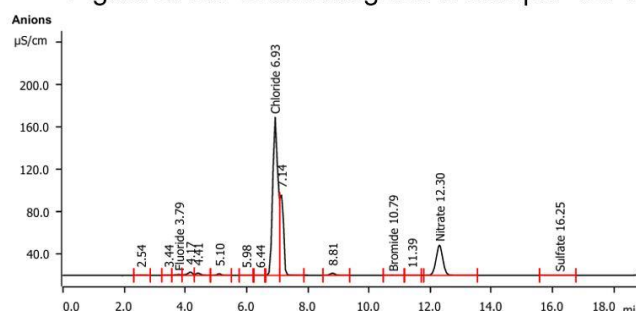| Sample ID	Retention time (min)	Area (µS/cm) x min	Concentration (ppm)
'PT'	12.79	817.253	9076.376
'CS-T'	12.30	7.271	80.418
'ED-T'	12.26	9.416	104.233
'CS-N'	12.397	0.1738	1.590
'ED-N'	12.235	0.3909	4.001

Figure 2: Ion Chromatogram of sample 'PT'

Figure 3: Ion Chromatogram of sample 'CS-T'
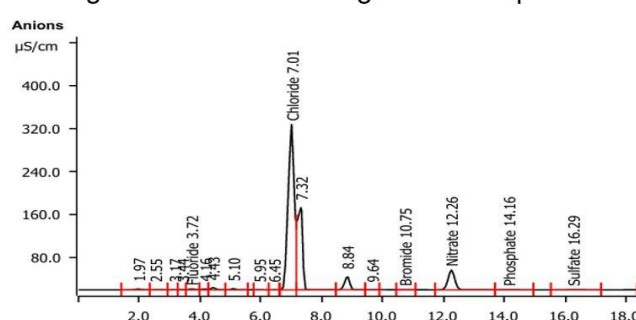

Figure 4: Ion Chromatogram of sample 'ED-T'
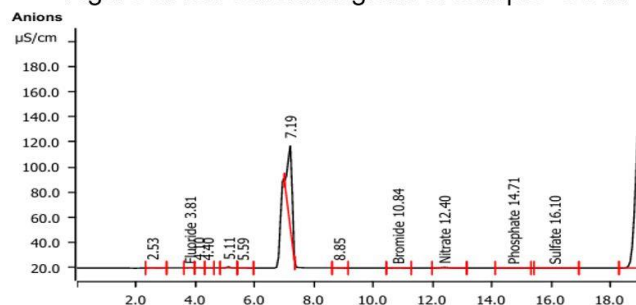

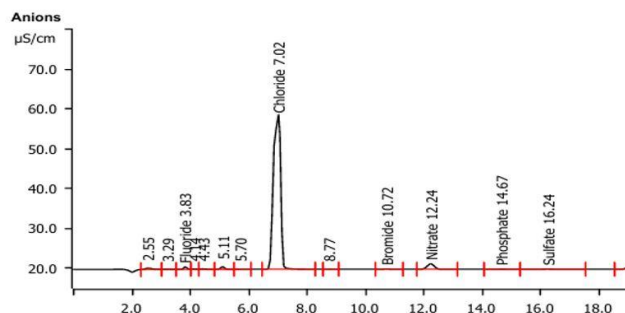Figure 5: Ion Chromatogram of sample 'CS-N'

Figure 6: Ion Chromatogram of sample 'ED-N'

4. Results and Discussion

Retention times of Nitrate ions in the samples 'PT', 'CS-T', 'ED-T', 'CS-N' and 'ED-N' were found to be in alignment with that of the standard anion mix.

Nitrate ions were detected in 'control soils' as well as in the 'explosion debris along with pit soil'.

The Concentration of Nitrate ions detected in the 'Control Soil' at Talegaon and Nigadi were 80.418 ppm and 1.590 ppm respectively, which is comparatively very different than each other.

The concentration of Nitrate ions detected in unexploded pyrotechnic (PT) was 9076.376ppm,

The concentration of Nitrate ions detected in the 'Explosion Debris Along With Pit Soil' at Talegaon and Nigadi was 104.233 ppm and 4.001 ppm respectively. Although the same pyrotechnic was exploded at both sites, the concentration of nitrate ions detected in the explosion debris and pit soil was substantially different at different site.

5. Conclusion

Nitrate ions are present in form of background concentration in the soils. Usually pit soils are collected for detection of nitrate ions from the residues of suspected explosive composition. However the forensic analyst must know that a positive result of testing such a pit sample may not always be just because of the explosive residues from the explosive composition. The nitrate ions naturally present in the soil or present due to fertilizers will contribute in the form of background concentration and may give a false positive result. Hence it is necessary to quantify the results of the exhibit and its related control soil to avoid false results. Quantification of the control sample will give an idea about the extent of background concentration of the nitrate ions, if any.

However, this background concentration is not same for different places. Hence any two sites are expected to have differing background concentration of Nitrate Ions and this must be taken into consideration while comparing the exhibits recovered from two different locations associated with the same or connected crime committed by same perpetrators.

Unexploded explosive devices/ compositions have higher response in the test methods due to unutilised explosive ions present in them. But once the explosive device/composition is exploded, maximum

amount of the residues gets utilised in the rapid combustion reaction and are converted to gaseous and non-gaseous products, whereas only a trace level of explosive residues are left back as unexploded form. Detection of such trace levels of residues requires highly sensitive and selective methods such as Ion Chromatography which can distinguish the response of the trace explosive residue and that of the background residues from surrounding by quantification.

Same explosive device/ composition when exploded at different locations and different times will be governed by differing parameters of explosive reaction and surroundings conditions. Hence the amount of explosive residues left after the explosion phenomenon will be considerably different.

Thus the above conclusions may guide a forensic analyst in making proper interpretation of the results obtained from systematic analysis of both the exhibits and its controls in order to avoid false and inconclusive results.

Conflict of interest
The authors declare that they have no conflicts of interest.

Acknowledgements

References

1. S. L. Lancaster and M. Marshall and J. C. Oxley, Laboratory Analysis of Explosion Debris, in: Wiley Encyclopedia of Forensic Science, **2014**, 1-43.
2. H. E. Hutson and E. McGee, Introduction to the Forensic Analysis of Intact Explosives, in: Forensic Analysis of Fire Debris and Explosives, **2019**, 193–225.
3. N. Abdul-Karim, C. S. Blackman, P. P. Gill, E. M. M. Wingstedt and B. A. P. Reif, Post-blast explosive residue – a review of formation and dispersion theories and experimental research, RSC Adv., **2014**, 4, 54354–54371.
4. D.K. Kuila, A. Chakrabortty, S.P. Sharma and S.C. Lahiri, Composition profile of low explosives from cases in India, Forensic Science International, **2006**, 159, 127–131.
5. C. Johns, R. A. Shellie, O. G. Potter, J. W. O'Reilly, J. P. Hutchinson, R. M. Guijit, M. C. Breadmore, E. F. Hilder, G. W. Dicinoski, P. R. Haddad, Identification of homemade inorganic explosives by ion chromatographic analysis of post-blast residues, Journal of Chromatography A, **2008**, 1182, 205–214.
6. D. Kumar, P. U. Kotawadekar, R. Das, Trace Analysis of Nitrate Content in Soil Samples using Ion Chromatography from Forensic Perspective, IJSREM, **2025**, 9(4), 1-9.
7. F.G.M. Mauricio, V.R.M. Abritta, R. de Lacerda Aquino, J.C. L.Ambr´osio, L. P.L. Logrado, I. T. Weber, Evaluation of Interferers in Sampling Materials Used in Explosive Residue Analysis by Ion Chromatography, Forensic Science International, **2019**, 307, 109908.
8. G. W. Dicinoski , R. A. Shellie & P. R. Haddad Forensic Identification of Inorganic Explosives by Ion Chromatography, Analytical Letters, **2006** 39:4, 639-657.
9. D.J. Klapec, G. Czarnopys, J. Pannuto, Interpol review of the analysis and detection of explosives and explosives residues, Forensic Science International: Synergy 6, **2023**, 100298.

10. U. K. Ahmad, O. S. Tze, M. F. Ghazali, Y. C. Hooi, M. K. Abdullah, Analysis Of Anionic Post-Blast Residues Of Low Explosives From Soil Samples Of Forensic Interest, The Malaysian Journal of Analytical Sciences, **2011**, 15(2), 213 – 226.
11. U. K. Ahmad, C. Y. Liew, M. A. M.Huri, S. A. A. S. Abdullah, Forensic Analysis of Inorganic Anions from Post Blast Pyrotechnic Residues, Jurnal Teknologi (Sciences & Engineering), **2013**,62(3), 77–82