Trace Analysis of Nitrate Content in Soil Samples using Ion Chromatography from Forensic Perspective

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Abstract - Soil samples are often sent to Forensic Science Laboratories (FSLs) as exhibits to determine the presence of explosive residues in post-blast cases. This work focuses on the trace analysis of nitrate ion (NO_3^-) content in the soil samples using Ion Chromatography (IC), an essential technique for inorganic explosives ion detection and confirmation. Soil was collected from the Talegaon area in Pune for spiking the standard case sample and to use as control soil to compare and find out the homogeneity of explosive content in the soil matrix. Soil samples of varying quantities - 50g, 40g, 30g, 20g and 10g were collected to assess the minimum sample mass required for reliable nitrate ions detection. A sensitive ion chromatographic method was used to detect the presence of nitrate ions. The findings provide crucial insights into the sampling and threshold soil mass necessary for the analysis of nitrate ions in trace amounts. Our study aligns with the development of standardized forensic protocols for explosive residue identification in post blast soil samples.

Key Words: forensic, trace analysis, explosive, soil, ion chromatography, nitrate ion.

1. Introduction

1.1. Background of forensic explosive analysis in soil

Explosives play a crucial role in various industrial, military, and criminal activities, making their forensic investigation an essential aspect of security and law enforcement [1-3]. Forensic soil analysis involves the examination of soil samples to aid in criminal investigations. It is based on the principle that soil is a unique, non-homogenous and variable material that can affect the detection of inorganic explosive residues due to its matrix effects. Among the diverse classes of explosives, nitrate-based explosives such as ammonium nitrate, ammonium nitrate fuel oil (ANFO), urea nitrate, potassium nitrate mixtures, etc., are widely used due to their availability, cost-effectiveness, and explosion potential. The forensic examination of post-blast residues is critical for identification of the trace elements in explosive ingredients used, reconstructing the blast event, and linking suspects to the crime scene [4-7].

1.2. Importance of nitrate detection in post-blast scenarios

Among various chemical markers, nitrate detection is particularly significant because nitrates serve as oxidizers in many explosive formulations, such as ammonium nitrate, ammonium nitrate fuel oil (ANFO), urea nitrate, potassium nitrate-based mixtures, etc.,. The identification and quantification of nitrate residues provide valuable information for a forensic examination report, aiding in criminal investigations, counterterrorism efforts, and environmental assessments [8,9].

1.3. Objectives of the study

The primary objective of this study was to develop a reliable and sensitive method for the trace analysis of nitrate content in the post-blast soil samples using Ion Chromatography (IC) to enhance forensic investigations. The study was conducted to optimize sample collection for post-blast soil samples and to check the effectiveness of Ion Chromatography (IC) as a precise analytical tool for detecting and quantifying nitrate ions in post-blast soil samples.

2. Materials and Methods

Soil sample collected were nearby area of the Central Forensic Science Laboratory (CFSL), Talegaon, Pune; Demineralised water (DM) procured from Labogen Fine Chem Industry, Ludhiana; Syringe filter (0.22 μm); and Filter paper procured from Clairofilt (India), Bhiwandi.

For Ion Chromatography, standard solution of inorganic anions (F^-, Cl^-, NO_2^-, SO_4^{2-}, PO_4^{2-}) were prepared from the 10 ppm stock solution from Sigma Aldrich (Switzerland) to standardize the instrument. The eluent 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. Regeneration solution for suppressor was prepared using analytical grade sulfuric acid solution obtained from Sigma Aldrich (Switzerland); The IC system used was Metrohm Advanced IC system by Metrohm Ltd. (Herisau, Switzerland); Metrosep A Supp 19 anion exchange column of hydrophilic polystyrene/divinylbenzene copolymer with quaternary ammonium groups was used for the analysis.

2.1. Methodology for obtaining spiked soil samples

To carry out spiking of soil and control soil, within 10m radius in an agricultural land from Talegaon Pune was chosen for soil sample collection. The soil was collected carefully in an self-sealing polythene packet using spatula to avoid any contamination and the collected samples were kept for drying overnight under normal atmospheric condition at room temperature.

2.2. Sample collection and preparation

For spiked samples, the collected bulk soil sample was divided into five portions of 50gm each. They were labelled as A, B, C, D and E. 0.25 gram of case exhibit containing nitrate ions was spiked into each of the samples (A, B, C, D & E) and thoroughly mixed to ensure homogenous distribution of the case exhibit. Weighed portions of the samples were taken for further analysis - 50gm of A (labelled as A1), 40gm of B (labelled as B1), 30gm of C (labelled as C1), 20gm of D (labelled as D1), and 10gm of E (labelled as E1). The same method followed for collection for control samples of A1 to E1.

For extraction of nitrate ions from the soil samples, DM Water was added into beakers containing the weighed portions as follows – 100ml each for A1, B1, C1, D1, E1 and its control soil samples (A1 to E1). The extracts were subjected to filtration using filter paper. The samples A1 to E1 were washed thoroughly with 100ml of DM water, twice, to collect nitrate content completely and the filtrates collected from samples (A1 to E1) were evaporated to dryness. It was then reconstituted in 100ml of DM Water and mixed to ensure uniformity. The same method was followed to control samples and 0.25 grams of case exhibit sample was taken as standard. Syringe filtration was conducted to remove minute impurities and 1ml of the filtrate was collected for each sample. It was further diluted ten times of its volume using DM Water. The diluted extract was used for IC analysis of nitrate ions.

2.3. Methodology used in Ion Chromatography

The IC system comprised of Methrohm 830 IC interface, 819 IC detector (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 Na2CO3 + 0.25mM NaHCO3 [12].

3. Observation

Table 1: Data obtained from ion chromatography

Sample ID	Sample Quantity (g)	Retention time (min)	Area (µS/cm) x min	Height (µS/cm)	Observed Conc. (ppm)
Case Standard	0.250	11.872	114.0921	293.656	1266.809
Sample A1	50	11.875	80.1746	230.933	890.108
Sample B1	40	11.555	61.4656	197.083	682.320
Sample C1	30	11.570	51.3171	171.249	569.606
Sample D1	20	11.650	42.7717	78.391	474.698
Sample E1	10	11.630	18.2764	428.265	202.644

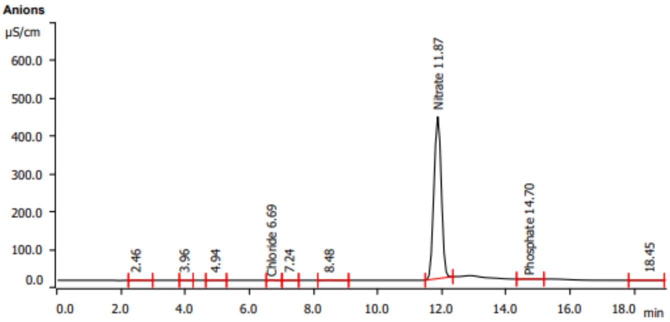
Table 2 : Effect of soil matrix in the Nitrate concentration

Sample ID	Sample Quantity (g) A	Observed Conc. of Control (ppm) B	Probable Conc. of the Std in the Spiked Sample (ppm) $C^{\#}$	Expected Conc. (ppm) D	Observed Conc. (ppm) E	Recovered Conc. (%) $F^{\$}$
Case Standard	0.250	NA	1266.809	1266.809	1266.809	100
Sample A1	50	9.281	1266.809	1276.09	890.108	69.753
Sample B1	40	11.251	1013.447	1024.698	682.320	66.587
Sample C1	30	8.656	760.085	768.741	569.606	74.096
Sample D1	20	3.594	506.724	510.318	474.698	93.020
Sample E1	10	4.967	253.362	258.329	202.644	78.444

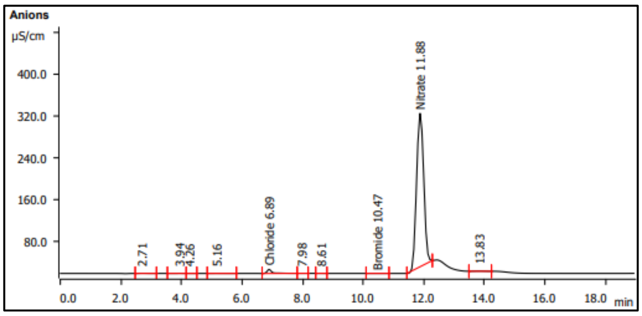
C = 1266.809*A/50 for samples A1 to E1. D = B+C. $ F = 100-((D-E)*100/D)

Figure 1 (a to f): Chromatograms obtained from spiked soil samples and standard through IC

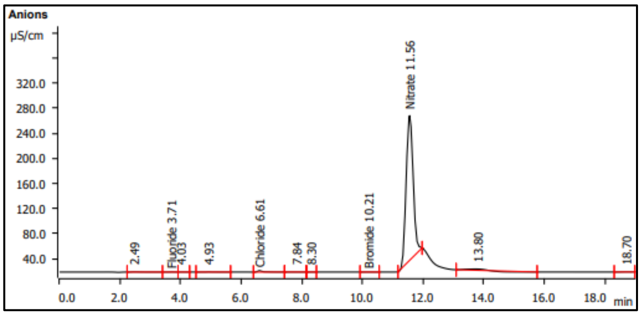
(a) Case Exhibit sample (Standard)



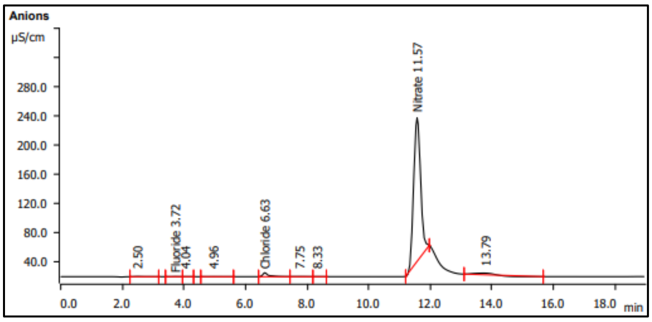
(b) Sample A1



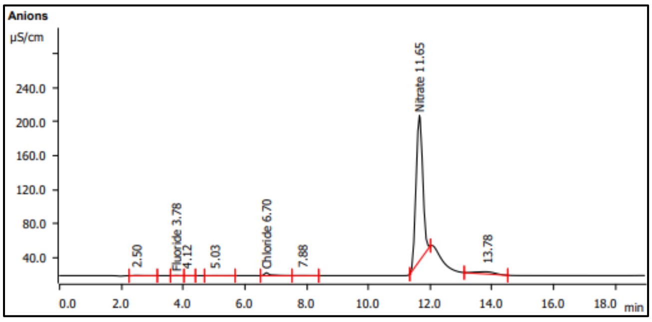
(c) Sample B1



(d) Sample C1



(e) Sample D1



(f) Sample E1

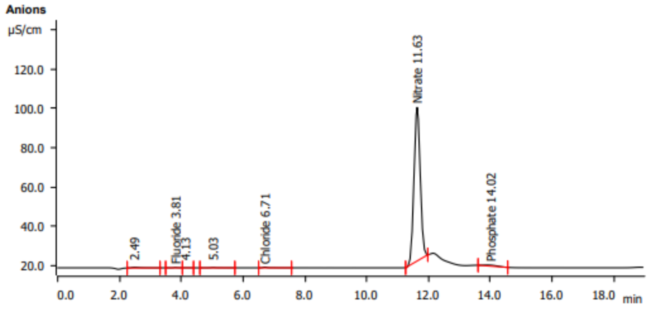
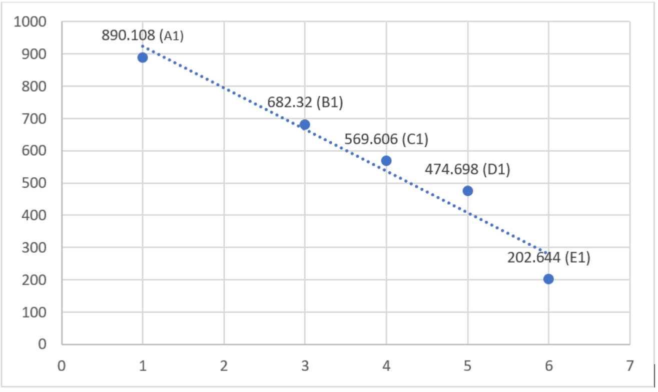


Figure 2: Scatter plot showing nitrate recovery from different amount of soil



4. Results and Discussion

The concentration of nitrate ion was found in the spiked soil samples were 890.108, 682.320, 569.606, 474.698, and 202.644 ppm for sample A1, B1, C1, D1, and E1 respectively. The concentration of the nitrate content in the case exhibit (Standard) sample was 1266.809 ppm.

The concentration of the nitrate content in the control soils for the above samples were 9.218, 11.251, 8.656, 3.594 and 4.967 ppm.

The Table-2 gives the detailed calculation of the probable concentration of the nitrate in the spiked soil sample, expected concentration of the nitrate and observed concentration of the same. It was observed that only 66.587% to 93.020% of nitrate concentration were recovered from the spiked soil samples A1 to E1. Remaining 6.980% to 33.414% of the nitrate content were not recovered from the soil due to it's matrix effect. Further observed that there was no uniformity in the concentration as per the order of the sample taken from 50g to 10g even though the spiked soil samples were thoroughly mixed.

To enhance forensic investigations, laboratories should adopt comprehensive sampling strategies, implement robust analytical techniques, and ensure proper documentation to maintain the integrity of evidence. These measures will improve the reliability of post-blast residue analysis and contribute to more accurate forensic conclusions.

5. Conclusion

Forensic trace analysis of post-blast soil samples presents several challenges, including sample heterogeneity, contamination risks, and the degradation of explosive residues due to environmental factors. Handling such samples requires standardized protocols to ensure the accurate detection and identification of explosive materials.

The homogenous nature of pit soil is under question. This study indicates the amount of soil sample to be collected for analysis of ions. Thus, appropriate sample collection is crucial for forensic analysis of explosives.

There is a scope for further research focusing on control soil sample collection in such cases. Optimization and validation studies can also be conducted for standardization of the method.

Conflict of interest

The authors declare no conflict of interest.

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BIOGRAPHIES

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