Analytics of Explosives

Analytical Strategy, HS 16
Anne Schuhmacher, Caterina Bernasconi, Dario Schmid

Expert: Dr. K. Schlatter, Scientific Research Service (SRS)
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1. Introduction

Where to look for explosives?

- Airport security control
- Quality control in production
- Forensic examination
- Demining

What to detect in an explosion incident?

- Who is responsible for the explosion?
- What was the explosive?
- Where was the source of the explosion?
- How was the bomb built?
1. Introduction

Explosion process

Explosion

After ignition, decomposition, production of gas and heat as well as a fast expansion of matter is observed.

Deflagration

The expansion and decomposition take place at a speed slower than the speed of sound.

Detonation

The expansion and decomposition take place at a speed faster than the speed of sound.
1. Introduction

Classification:

- Organic explosives
  
  Nitro compounds
  
  ![Nitro compounds](image)
  
  Nitroglycerin
  Trinitrotoluene (TNT)
  Hexogen
  Triacetonetriperoxide (TATP)

- Inorganic explosives
  
  Salts
  
  ![Salts](image)
  
  Chlorates
  Perchlorates
  Nitrates

  Black powder: KNO₃, S, C
  
  Elemental sulfur
  Red phosphorus
2. Gathering Evidence

Trackhounds

**Principle:** Dogs can be trained on explosives in order to detect them at an explosion incident

**Sensitivity:** very good
- Laboratory experiments: 2,4-dinitrotoluene ≥ 500 ppt
- Nitroglycerin ≥ 10 ppb

**Specificity:** extremely good
- Laboratory experiments show very good discrimination of components
- Equilibrium between specificity and generalization needed

**Dynamic Range:** „tracking-to-source“

**Advantages:**
- Very sensitive and specific
- Rather inexpensive

**Drawbacks:**
- No determination of the substance
- Skilled handler and dog necessary
2. Gathering Evidence

Test kits – colorimetric methods

Principle: The reaction of a specific explosive with a specific reagent leads to a color change indicating the presence of the explosive.

Detection of nitroaromatic explosives, e.g. TNT
- Nitroaromatic compounds form coloured products in presence of alkalis
- Example: Janowski reaction

\[
\text{NO}_2^– + \text{KOH(aq)} \rightarrow \text{NO}_2^– + \text{H}_2\text{O}
\]

Detection of nitrate esters, e.g. Nitroglycerol
- Detection based on detection of NO\(_2^–\) ions formed during the reaction
- Example: Griess reaction

\[
\text{R} - \text{O}^– + \text{H}^+ \rightarrow \text{R} = \text{O}
\]
2. Gathering Evidence

Test kits – colorimetric methods

Detection of peroxide-based explosives, e.g. TATP

- Detection via enzymatic methods
- Example: Oxidation of ABTS

Detection limit for TATP: $8 \times 10^{-6}$ mol/L

Test Kits for Field Tests

- Field tests are carried out as preliminary examination on the site of explosion
- Several kits based on the colorimetric tests for different explosives
2. Gathering Evidence

Flame coloration test

Principle: Different cations lead to different coloration of the Bunsen burner flame. Method gives an idea, if or which cations are in the sample.

Coloration:
3. Sampling and Sample Preparation

Sampling

What are the samples?

• Explosion mostly leads to big destruction => sampling difficult

• Mostly: the intact explosive itself is not found

• Sampling of exploded material, e.g. the container of the bomb

Important aspects while sampling

• Traces should not get lost
  => careful packaging and wiping of the sample

• Safety
3. Sampling and Sample Preparation

Sample Preparation for Organic and Inorganic Compounds

Liquid Extraction

• Wipe containing organic and/or inorganic sample

• Extraction of the wipe with solvent ethanol/water
  → organic as well as inorganic compounds recovered in good yield

• Extraction with organic solvent and pure water
  → separation of organic and inorganic compounds
3. Sampling and Sample Preparation

Sample Preparation for Organic Explosives

Supercritical fluid extraction

- Extraction of the explosive from a sample support, e.g. soil or wipe
- Principle:
  - Recovery of explosives good with ≥ 60% with pure CO₂
4. Analytical Methods

Methods for organic explosives

- GC/LC-MS

**Spectrometers:** Quadrupole and ion trap
**Ionization methods:** ESI, APCI

**Identification** through characteristic fragment ions

**Advantages:**
- can be miniaturized
- sensitivity
- selectivity
- speed of the analysis
- LC-MS: analysis at room temperature

**Drawbacks:**
- Costs
- Complexity
4. Analytical Methods

Methods for organic explosives

- **GC-MS: Example**

  Mixture of explosives (10 ppb each)

  **Experimental:**

  - liquid-liquid extraction from H₂O
  - x100 concentration
  - NICI
  - **Detection limits:** 0.18-1.11 ng
4. Analytical Methods

Methods for organic explosives

- Ion Mobility Spectroscopy

How it works:
- Sampling with cloth strip
- Heating to 200°C
- Ionization
- Electric field: 200 V/cm
- Detector → electric signal
- Identification: characteristic ions

Advantages:
- Low limits of detection (pg)
- High selectivity
- Ambient pressure
- Simple instrumentation & low maintenance
- Fast, Portable, Inexpensive

Disadvantages:
- Need for human work

Limits of detection: pg
4. Analytical Methods

Methods for organic explosives

- Ion Mobility Spectroscopy: more in detail

Sampling:
Difficulty: large air volumes as sample → preconcentration necessary:
air drawn through a metal mesh where the sample accumulate

Ion formation:
Reaction of the sample with a reservoir of ions

Ion sources:
- 10 mCi $^{63}$Ni
- ESI
- Electric discharge
- Photoinitiation
4. Analytical Methods

Methods for organic explosives

- **Amplified Fluorescent Polymers**

  **How it works:**
  - Introduction of sample in a conjugated polymer
  - Fluorescence induced by irradiation with UV/Vis
  - Analyte binds to a conjugated fluorescent polymer \(\rightarrow\) **Fluorescence Quenching** (FQ)
  - Photodetector: diminution of the emission intensity indicates that the analyte is present.

Explosives (TNT, DNT) very electron deficient (A): readily accept electrons from excited fluorophores (D)

![Diagram showing energy levels and electron transfer]

**Amplification of the signal:**
Binding of a single analyte molecule quenches the fluorescence of the whole polymer.
4. Analytical Methods

Methods for organic explosives

- **Amplified Fluorescent Polymers**

  **Selectivity:**
  - Fluorescence quenching only efficient with favourable reduction potential: $E_{\text{red}} > -1.52\text{eV}$
  - Vapor pressure can lead to different temporal responses

  **Thin-film conjugated polymers:**
  - Easier to use
  - No influence by solvation or diffusion
  - Even better amplification
  - Problem: non-fluorescent aggregates have to be avoided

  **Advantages:**
  - Properties tunable through side groups
  - High sensitivity
  - Selectivity

  **Drawbacks:**
  Only explosives with a suitable reduction potential can be detected.
4. Analytical Methods

Methods for organic and inorganic explosives

- **ED-XRF**

  - Irradiation of the sample with X-ray
  
  - Excitation of electrons in energetically low lying orbitals (closed shells)
  
  - Relaxation of electrons in higher lying orbitals (valence shell)
  
  - Characteristic bands of the element

- Application for surface analysis after explosions
- Exists as a portable device

https://www.911metallurgist.com/blog/portable-xrf-analyzer-price; retrieved: 22/11/16
4. Analytical Methods

Methods for organic and inorganic explosives

• IR / Raman Spectroscopy

  strong characteristic absorptions in the IR region

Example: R-NO₂ :
- Diagnostic value: is there a nitro peak?
- λ depends on the type of atom to which the nitro group is directly attached
- E.g. C-NO₂: νₚₛ ≈ 1590 – 1510 cm⁻¹, νₛ ≈ 1390 – 1320 cm⁻¹;

Analysis of mixtures:
- IR can identify the components
- Spectrum of a known component can be artificially subtracted
- Previous separation

Ambiguous identification:
Combination with retention data from chromatographic methods

IR spectrum of TNT

4. Analytical Methods

Methods for organic and inorganic explosives

- **IR / Raman Spectroscopy**

  **Advantages:**
  - Portable
  - Easy to use, low maintenance
  - Non-destructive
  - Fast
  - Small amount of sample necessary & small sample preparation

  **Drawbacks:**
  - Less sensitive than MS (→ IR not so suitable for trace analysis)
  - IR: very sensitive to moisture
  - Raman: Fluorescence
  - NIR can burn dark substances

  **Limit of detection** \( \geq 1 \) mg

4. Analytical Methods

Differential Reflection Spectroscopy (DRS)

- Light source – UV (or visible or near infrared)
- Detection – reflectivity of the surface of the inspected area
- Each material has a unique electronic structure
- LOD: \(10^{-7}\) g to \(5 \times 10^{-5}\) g depending on the method/set-up parameters

Fingerprint for identification of substance Using curve discrimination programs.

Advantages:
- Contact-less
- Fast
- Differentiation between explosives

Drawbacks:
- Surface measurements only

The technique can be developed into a device that is lightweight, rugged, and small.

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T. Dubroca, G. Brown, R.E. Hummel, Optical Engineering 53(2), 021112 (February 2014)
4. Analytical Methods

Methods for inorganic explosives

- **General**

  Reminder: chlorates, nitrates, nitrites, ...

  Measurement assurance: Need positive results from two independent tests.

- **Spot tests** (e.g. Griess test for nitrite)

- **Ion Chromatography (IC)**

- **Capillary Electrophoresis (CE)**

- **IR Spectroscopy**

  results of the spot tests or the infrared spectra can be inconclusive or unsatisfactory → IC or CE useful
4. Analytical Methods

Methods for inorganic explosives

- **Ion Chromatography**

  Ion separation:
  - Nice for many anions (importantly chlorate from nitrate)
  - Difficulties with late eluting peaks
  - Complex interactions of ions with stationary phase
  - Need peak identity confirmation (2nd measurement needed)

Detection:
  - Conductivity of eluent suppressed by corresponding acids of measured anions (modification by column)
  - Linear dynamic range:
    - chlorate, nitrate: 10 – 200 ppm
    - nitrite: ~ 100 ppm
  - Limit of Detection: ~ 2 ppm

Figure 1. A sample ion chromatogram showing some anions of interest: (1) Cl\(^-\) 5ppm, (2) NO\(_3^-\) 10ppm, (3) ClO\(_3^-\) 25 ppm, (4) NO\(_2^-\) 25ppm, (5) SO\(_4^{2-}\) 30ppm.

Figure 2. Calibration curves for nitrate, nitrite and chlorate.
4. Analytical Methods

Methods for inorganic explosives

- **Capillary Electrophoresis**

  Ion separation:

  - Nice for many anions
  - Plate number up to 70’000 (vs. 3’000 for IC)
  - NO difficulties with late eluting peaks
  - Difference in charge to mass ratio of solvated ions
  - Ion mobility: induced or electroosmotic flow

Inverse photometric detection:

- Anions cause loss in absorbance of the eluent at certain wavelengths (e.g. 280 nm, dichromate)
- Linear dynamic range: 1 – 50 ppm
- Limit of Detection: ~ 0.5 ppm
- Peak identity confirmation:
  - second analysis with detection at a lower wavelength

Figure 2. Anion Standard Containing Ions Present in Explosive Residue. Analysis performed at 205 and 280 nm using Capillary Electrophoresis. Peak identification: 1-Cl\textsuperscript{-}, 2-NO\textsubscript{2}\textsuperscript{-}, 3-ClO\textsubscript{3}\textsuperscript{-}, 4-NO\textsubscript{3}\textsuperscript{-}, 5-SO\textsubscript{4}\textsuperscript{2-}, 6-SCN\textsuperscript{-}, 7-ClO\textsubscript{4}\textsuperscript{-}, 8-HCO\textsubscript{3}\textsuperscript{-}
4. Analytical Methods

Methods for inorganic explosives

- **IC and CE – Complementary Methods**

Excellent way to confirm peak identities:

- Differences in elution order → peak interferences easy to detect

Combine Advantages:

- High sensitivity (CE)
- Low limit of detection (CE)
- Wide concentration variety (IC)
- Broad analyte diversity (IC)

![Figure 3. Comparison of Elution Order in Capillary Electrophoresis and Ion Chromatography.](image-url)
5. Trace vs. Bulk Analysis

**Trace analysis**: look for a specific chemical from a library

**Bulk analysis**: analysis of a property indicative for an explosive

**Difference between trace and bulk analysis**

- Trace analysis: look for a specific chemical from a library
- Bulk analysis: analysis of a property indicative for an explosive

**Bulk analysis**

- Adavantage: No limitation to a library of compounds
- Drawback: Less specific, more false results possible

- Properties of explosives: high density, high oxygen- and/or nitrogen content, fast energy release

- Most important technique: X-ray analysis and X-ray computer tomatographic analysis
  - Analysis of density
  - Penetration of the sample with the x-ray smaller, the more dense the sample

- Sample can be extracted and diluted to proceed with the trace analysis procedures
6. Conclusion

- Diverse challenges in detection of explosives
- Broad variety of chemicals considered as explosive material
- Various methods for sample preparation and detection available
- Knowledge about the explosive can help to identify the criminals
6. Conclusion

Thank you for your attention!
Sources