

## TECHNICAL NOTE

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# Organic Explosives Analysis Using On Column-Ion Trap EI/NICI GC-MS with an External Source

**ABSTRACT:** In this study, a standard method by gas chromatography coupled with mass spectrometry (GC/MS) for the analysis of classical organic explosives was developed. This method was validated in the EI mode, based on the XPT 90-210 standard method (1). Detection limits (LOD) and quantitation limits (LOQ) were both determined using electronic impact (EI) and negative ion chemical ionization (NICI) modes. These were compared and results showed that in the NICI mode, detection limits were lower than in the EI mode, thus NICI mode appeared to be the best way to analyze nitrate esters. Results of ion trap MS detection were then compared with those obtained in a previous study (2) with single quadrupolar technology. Major ions that were obtained using ion trap MS detection in these two modes were reported.

**KEYWORDS:** forensic science, gas chromatography, ion-trap mass spectrometry, detection limits, organic explosives

Characterization of explosives residues in various matrices is often complicated because many analytes may interfere. Developing new methods to detect and identify explosives at low concentration in complex matrices is a real challenge for the analyst.

The variety and the number of explosives (mineral, organic) and different matrices (soils, wood, metal, sand, concrete, plastics . . .) require the analyst to tailor extraction methods, clean-up procedures (such as solid phase extraction SPE or solid phase micro extraction SPME) and new analytical methods.

Gas chromatography is very widely used in the field of explosives. Many selective detectors are available: electron capture detection (ECD), nitrogen compounds detection (NCD), thermal energy analyzer (TEA) or nitrogen phosphorus detection (NPD). Many laboratories are equipped with one or more selective detectors.

Although MS detection is universal and yield more information, it is often less sensitive than the aforementioned detectors. Moreover, the ability to carry out MS/MS experiments with triple quadrupolar or ion-trap MS detectors is a great advantage (the identification of detected explosive can be confirmed). Some explosives are thermally unstable, in particular, nitro esters (3–5). In this study, HMX was not submitted. Indeed, our method was not suited to its analysis.

Mass spectrometry is perfectly suited for trace analysis of explosives in residues because of its specificity and sensibility. The EI mode is the most widely used; however, NICI appeared to be a softer ionization technique for explosives. It is preferable that molecu-

lar species with lower internal energy are formed. The ionization process is performed by introducing a reagent gas in the source. The identification is easier because of the presence of molecular ions (6).

In this study a new detection method for most common organic explosives (nitro aromatics, nitro esters and nitramines) is presented. Detection limits (LOD) and quantitation limits (LOQ) were worked out, based on the XPT-90 210 French AFNOR standard (1) (the latter provides statistical tools characterizing the performance of an analytical method in terms of linearity, repeatability, reproducibility as well as detection and quantitation limits). Results are given for the EI and NICI modes.

In NICI mode, two different reagent gases were tested: isobutane and methane. This work allowed direct comparison between ion trap detection results and those determined in a previous study using single quadrupolar MS detection (2). The limits were determined in full scale mode. Selected ion monitoring (SIM) mode could certainly lower detection limits. The injection was performed directly on the analytical column with a dedicated on-column injector to prevent any degradation of the more unstable explosives (PETN, NG etc.) (2,7).

## Experimental Procedure

### Apparatus

GC/MS analyses were performed on a Thermo Finnigan® PolarisQ Gas Chromatograph/Mass spectrometer (Ion Trap) with an external source operating in two modes : electron impact (EI) and negative ion chemical ionization (NICI). Instrument operating parameters are given in Table 1. The GC was fitted with a 15 m RTX-5 MS column from Restek® with a 0.25 mm I.D. and 0.25 µm film thickness.

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TABLE 1—Mass spectrometry parameters.

|                                | EI     | NICI   |
|--------------------------------|--------|--------|
| Transfer line temperature (°C) | 250    | 180    |
| Electron energy (ev)           | 70     | 70     |
| Full scan mass range scanned   | 29–350 | 29–350 |
| Mass scan rate (scan/s)        | 2,5    | 2,5    |
| Reagent gas flow rate (mL/min) | NA*    | 1      |

\* NA = Not applicable.

TABLE 2—Chromatographic parameters.

|                            |                |
|----------------------------|----------------|
| Initial temperature (°C)   | 60             |
| Temperature increase (°C)  | 230            |
| Rate (°C/min)              | 15             |
| Flow rate (mL/min)         | 1,2            |
| Injection mode             | Cold on-column |
| Injection temperature (°C) | Not regulated  |
| Volume injected (μL)       | 1              |

### Reagents

Isobutane and methane were used as reagent gas in NICI mode. Ethyleneglycol dinitrate (EGDN) and pentaerythrol tetranitrate (PETN) were obtained from Cerilliant®. 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine (HMX) and tetryl were obtained from Supelco®. 3,4-dinitrotoluene (3,4 DNT) and nitroglycerine (NG) were obtained from Restek®. Standard solution concentration was 1g/L for all reagents. Stock solutions of 10 ng/μL were prepared by diluting down 100 fold the standard solution.

### Method

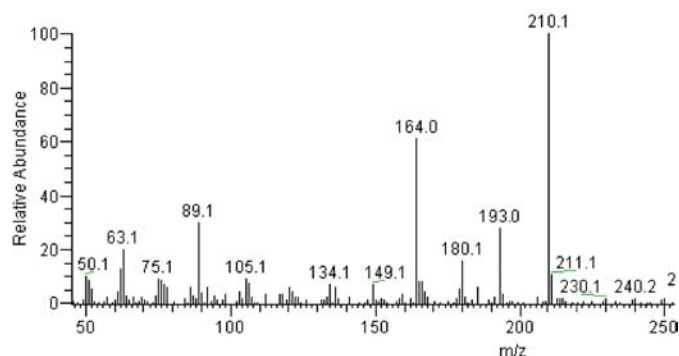
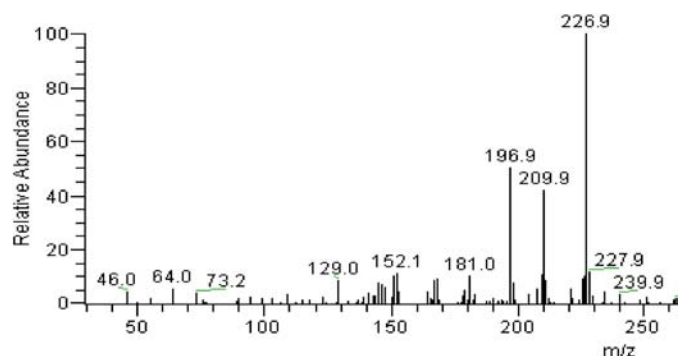
Chromatographic parameters are given in Table 2. Samples were directly introduced with a 10 μL syringe in the capillary column, manually, without any liner being used.

### Results and Discussion

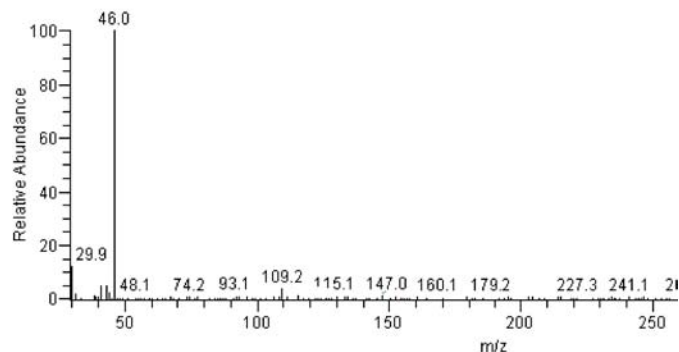
Linearity, detection limits (LOD) and quantitation limits (LOQ) were determined, based on the XPT-90 210 French AFNOR standard method. This is the evaluation protocol of an alternative analytical method compared to a reference method.

Major ions, whatever the ionization mode (EI or NICI), are given in Table 3. Mass spectra were also given for some explosives studied both in EI and NICI (Fig. 1a to 1f). Mass spectra were very different

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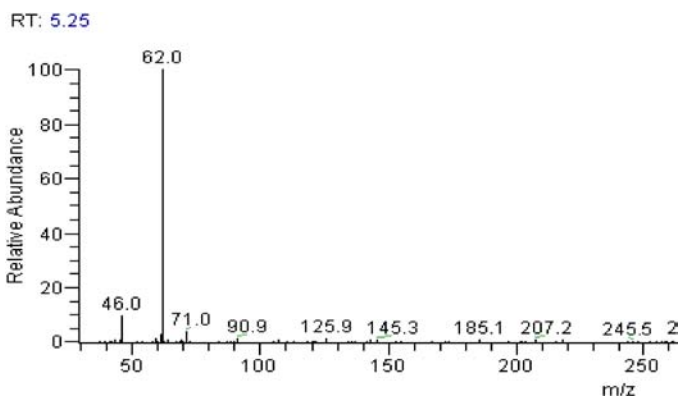
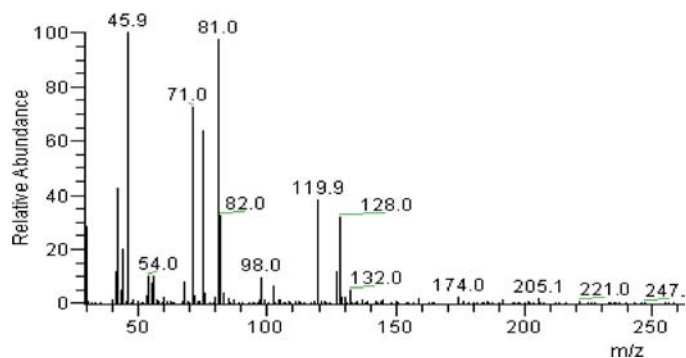
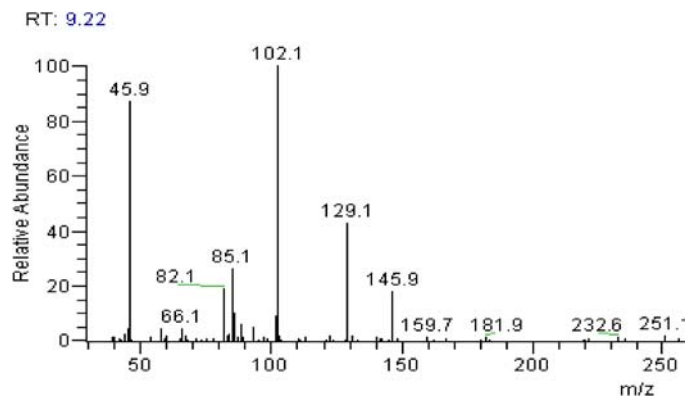
FIG. 1a—EI mass spectra of 2,4,6-TNT ( $M = 227$  amu).FIG. 1b—NICI mass spectra of 2,4,6-TNT ( $M = 227$  amu).

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FIG. 1c—EI mass spectra of NG ( $M = 227$  amu).TABLE 3—Observed ions ( $m/z$ ) in both modes (EI and NICI).

| Analyte | M (g/mol) | $m/z$                           |                                 |                             |
|---------|-----------|---------------------------------|---------------------------------|-----------------------------|
|         |           | EI                              | NICI (with isobutane)           | NICI (with methane)         |
| 2,4-DNT | 182.14    | 63/89/119/ <b>165</b>           | 46/165/ <b>182</b>              | 152/165/ <b>182</b>         |
| 2,6-DNT | 182.14    | 63/89/119/148/ <b>165</b>       | 46/ <b>152/182</b>              | 46/152/ <b>182</b>          |
| 3,4-DNT | 182.14    | 65/ <b>89/182</b>               | 46/ <b>152/182</b>              | 118/152/ <b>182</b>         |
| EGDN    | 152.06    | 30/43/ <b>46</b>                | 46/ <b>62</b>                   | 46/ <b>62</b>               |
| NG      | 227.09    | 30/ <b>46</b>                   | 46/ <b>62</b>                   | 46/ <b>62</b>               |
| PETN    | 316.14    | 30/ <b>46</b>                   | 46/ <b>62</b>                   | 46/ <b>62</b>               |
| RDX     | 222.03    | 30/ <b>42/46/75/120/128</b>     | 46/ <b>102/129</b>              | 46/85/ <b>102/129</b>       |
| TNT     | 227.13    | 63/89/164/ <b>210</b>           | 197/210/ <b>227</b>             | 197/210/ <b>227</b>         |
| TY      | 287.15    | 118/149/179/ <b>194/224/242</b> | 182/207/212/225/241/ <b>242</b> | 194/207/212/225/ <b>242</b> |

\* In bold: major ion.

FIG. 1d—NICI mass spectra of NG ( $M = 227$  amu).FIG. 1e—EI mass spectra of RDX ( $M = 222$  amu).FIG. 1f—NICI mass spectra of RDX ( $M = 222$  amu).

depending on the ionization process. In NICI mode, the nitroesters (EGDN, NG and PETN) yielded very few ions while in EI, ion  $[\text{NO}_2]^+$  (46) and ion  $[\text{NO}]^+$  (30) were observed. In EI mode, for TNT, 2,4-DNT and 2,6-DNT, ion  $[\text{M-OH}]^+$  was observed but not the molecular ion. The loss of OH radical was observed in all molecules having an H in ortho position. The molecular ion was only observed for the 3,4-DNT. For RDX, ion  $[\text{NO}_2]^+$ ,  $[\text{NO}]^+$  and  $[\text{CH}_2\text{N}(\text{NO}_2)_2]^+$  were present apart from the molecular ion. Except for 3,4-DNT, the molecular ion was not observed and very few diagnostic ions were produced in the EI mode.

During a chemical ionization (CI), ions react with molecules to ionize the analyte. This chemical ionization process starts when a (high pressure) reagent gas (either isobutane or methane) is ionized

TABLE 4—Detection and quantitation limits by GC/EI with manual injections.

| Analyte | LOD (ng)<br>S/B $\geq 5$ | LOQ (ng)<br>S/B $\geq 10$ | Reproducibility<br>(% RSD) | Conc. Range<br>(ng/ $\mu\text{L}$ ) |
|---------|--------------------------|---------------------------|----------------------------|-------------------------------------|
| 2,4-DNT | 0.2                      | 0.4                       | 9.8–14.9                   | 1.0–5                               |
| 2,6-DNT | 0.2                      | 0.4                       | 4.6–16.9                   | 1.0–5                               |
| 3,4-DNT | 0.7                      | 0.8                       | 5.9–11.8                   | 1.0–5                               |
| RDX     | 1.1                      | 1.8                       | 3.8–12.0                   | 6.0–14                              |
| TNT     | 0.5                      | 0.7                       | 9.4–13.7                   | 1.0–5                               |
| TY      | 1.8                      | 2.4                       | 4.2–12.2                   | 4.0–12                              |
| EGDN    | 1.6                      | 1.8                       | ND*                        | ND*                                 |
| NG      | 1.1                      | 1.6                       | ND*                        | ND*                                 |
| PETN    | 4                        | 8                         | ND*                        | ND*                                 |

\* ND: Not determined.

TABLE 5—Detection and quantitation limits by GC/NICI with isobutane and methane as reagent gases.

| Analyte | Isobutane<br>LOD (ng)<br>S/B $\geq 5$ | Methane<br>LOD (ng)<br>S/B $\geq 5$ | Isobutane<br>LOQ (ng)<br>S/B $\geq 10$ | Methane<br>LOQ (ng)<br>S/B $\geq 10$ |
|---------|---------------------------------------|-------------------------------------|--|--------------------------------------|
| 2,4-DNT | 0.6                                   | 0.2                                 | 0.8                                    | 0.3                                  |
| 2,6-DNT | 0.2                                   | 0.1                                 | 0.3                                    | 0.2                                  |
| 3,4-DNT | 0.3                                   | 0.1                                 | 0.4                                    | 0.2                                  |
| RDX     | 0.6                                   | 0.4                                 | 0.8                                    | 0.5                                  |
| TNT     | 0.3                                   | 0.1                                 | 0.4                                    | 0.2                                  |
| TY      | 0.6                                   | 0.3                                 | 0.7                                    | 0.4                                  |
| EGDN    | 0.2                                   | 0.6                                 | 0.4                                    | 0.7                                  |
| NG      | 0.6                                   | 0.6                                 | 0.7                                    | 0.7                                  |
| PETN    | 3.2                                   | 2.2                                 | 3.3                                    | 2.3                                  |

\* ND = Not determined.

by electron impact (a high reagent gas pressure results in ion-molecule reactions between the reagent gas ions and reagent gas neutrals). Resulting products can react with the analyte molecules to produce analyte ions.

The NICI mode helps fragmentations of heavy masses and often yields information on the molecular ion. Compared with EI, the fragmentation is reduced but library searching is still possible if a specific library was built. The most common CI reagent gases are methane, isobutane and ammonia. With isobutane as reagent, although not universal, adducts are relatively more abundant than in methane; the latter is well suited for most organic compounds and the fragmentation is more extensive.

A molecular ion was observed (ion at  $m/z$  227 for TNT and ion 182 for 2,4-DNT, 2,6-DNT and 3,4-DNT) for every nitroaromatic. For TNT, the ion at  $m/z$  210 was corresponding to  $[\text{M-OH}]^-$  and the ion at  $m/z$  197 was  $[\text{M-NO}]^-$ . For nitroesters, fragment ions 62  $[\text{NO}_3]^-$  and 46  $[\text{NO}_2]^-$  were observed. For nitramines, the ion at  $m/z$  129 was  $[\text{M-NO}_2\text{HNO}_2]^-$ , the ion at  $m/z$  102 was  $[\text{C}_2\text{H}_4\text{N}_3\text{O}_2]^-$  and the fragment at  $m/z$  46 was  $[\text{NO}_2]^-$ .

Table 4 shows the measured LOD and LOQ in EI mode. LOD were the lowest for 2,4-DNT, 2,6-DNT, TNT and 3,4-DNT. PETN showed the highest LOD. Results were very reproducible.

In Tables 5 and 6, results for NICI showed lower LOD for almost every explosive. Sensitivity improved, except for 2,4-DNT, with isobutane as reagent gas. Regarding nitroesters (NG and EGDN), sensitivity improved in an important manner. For nitramines and for nitroaromatics, LOD were lower but the sensitivity improvement is less important than for nitroesters.

NICI with methane as reagent gas showed better results except for EGDN where sensibility decreased and for NG where the sensitivity

TABLE 6—LOD comparison (in ng) for each explosive, both in EI and NICI modes.

| Analyte | LOD/EI<br>S/B $\geq 5$ | LOD/NICI<br>with isobutane<br>S/B $\geq 5$ | LOD/NICI<br>with methane<br>S/B $\geq 5$ |
|---------|------------------------|--|--|
| 2,4-DNT | 0.2                    | 0.6  | 0.2                                      |
| 2,6-DNT | 0.2                    | 0.2  | 0.1                                      |
| 3,4-DNT | 0.7                    | 0.3  | 0.1                                      |
| RDX     | 1.1                    | 0.6  | 0.4                                      |
| TNT     | 0.5                    | 0.3  | 0.1                                      |
| TY      | 1.8                    | 0.6  | 0.3                                      |
| EGDN    | 1.6                    | 0.2  | 0.6                                      |
| NG      | 1.1                    | 0.6  | 0.6                                      |
| PETN    | 4                      | 3.2  | 2.2                                      |

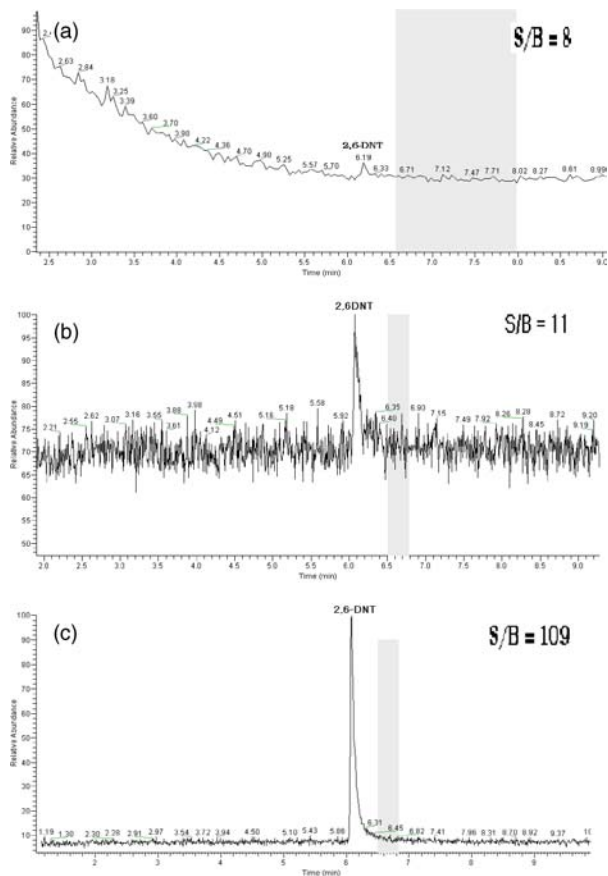


FIG. 2—Comparison of sensitivity between the two modes of ionization for 2,6-DNT at 0.2 ng: 2A: EI mode, 2B: NICI mode with isobutane, and 2C: NICI mode with methane.

is the same. A chromatogram is shown in Fig. 2. Replacement of isobutane reagent gas by methane improved the sensitivity (about ten fold for the 2,6-DNT as shown in Fig. 2).

Our study showed the benefits from an external ionization source. The ionization process was separated from mass analysis; reactions between ions and molecules occurred less often. Negative ion chemical ionization is a very interesting way to analyse organic explosives.

Further experiments will have to be carried out. The chemical ionization in positive mode (PCI) was not yet assessed with our external source. The PolarisQ in Pulsed Positive Ion Negative Ion Chemical Ionization (PPINICI) mode offers the ability to detect both positive and negative ions in a single scan. This can be very interesting to screen rapidly samples for explosives. In the future, MS/MS experiments after NICI or PCI/NICI will be assessed. Reference libraries in both EI and NICI ionization were built.

## Conclusion

A method to detect the most common organic explosives (nitro aromatics, nitro esters, and nitramines) by on column ion-trap GC/MS with an external source was developed. This method (in EI mode) has been partially validated using XPT 90-210 standard. LOD and LOQ were determined with precision. The limits appeared to have improved compared with previous results, obtained by means of single quadrupolar GC/MS. NICI mode was more sensitive than EI mode and well suited for the analysis of nitro-esters (EGDN, PETN and NG). The first NICI experiments showed that methane was a better reagent gas than isobutane. In the future, more experiments will be carried out by means of MS/MS after NICI. As an interesting alternative, NICI and PCI could be swapped during the same analysis.

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