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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY OF EXPLOSIVES

J. YINON* and D.-G. HWANG
Department of Isotope Research, Weizmann Institute of Science, Rehovot (Israel)
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SUMMARY

A series of explosives were studied by combined high-performance liquid chromatography–mass spectrometry (HPLC–MS). Separations were done on a C_8 reversed-phase column, using acetonitrile–water and methanol–water as mobile phases, followed by UV and mass spectrometry (MS). The MS analysis was carried out on-line, using a direct liquid insertion probe LC–MS interface. The chemical ionization mass spectra obtained included mainly protonated molecular ions, adduct ions and typical fragment ions which made positive identification of the compounds possible.

INTRODUCTION

The analysis of explosives has become of major importance in several applications. In the forensic identification of explosives, the analysis of post-explosion residues is important in the investigation of a bombing because it can help connect the type of explosive used with a suspect. The results of the analysis are also needed as evidence in court.

In the environmental analysis of explosives, the analysis of water contaminated by explosives has become necessary because of the discharge of waste waters produced in the manufacture of ammunition and the contamination of underground water resulting from the burial of obsolete ammunition and explosives in the soil.

As many explosives are toxic, inhalation of their vapours presents a health hazard. It is therefore important periodically to analyse blood samples of personnel working in munitions manufacturing plants for traces of explosives and their metabolites.

A variety of methods and techniques have been used for the analysis of explosives[1]. In most applications an analytical method is required that combines good separation characteristics with highly specific and sensitive detection. The liquid chromatography–mass spectrometry (LC–MS) system has such characteristics and has the advantage over gas chromatography–MS that it is suitable for thermally sensitive and involatile compounds.

High-performance liquid chromatography (HPLC) has become a widely used separation technique for explosive mixtures[1–4], and mass spectrometry is a sensitive

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and specific method for the detection and identification of explosives[1–5].

Several LC–MS systems have been used successfully for a variety of applications[6–9]. Initial results have been obtained using LC–MS for the analysis of explosives with negative-ion chemical ionization[10]. This paper describes the use of an LC–MS system for the separation and identification of a variety of technical and standard explosive mixtures using positive-ion chemical ionization (CI).

EXPERIMENTAL

Equipment

The HPLC system consisted of an Eldex A-30-S pump (Eldex Labs., Menlo Park, CA, U.S.A.), an Eldex CMT-II solvent programmer, an Eldex LP-II low-pressure valve, a Rheodyne 7125 sample injector (Rheodyne, Cotati, CA, U.S.A.) and a Waters 441 UV detector (Waters Assoc., Milford, MA, U.S.A.). The HPLC column used was an RP-8 (C_8) reversed-phase column containing LiChrosorb, particle size 10 μm (10 cm $\times$ 4.6 mm I.D.) (Brownlee Labs., Santa Clara, CA, U.S.A.). The mobile phases were methanol–water (1:1) and acetonitrile–water (1:1), and the flow-rate was 1 ml/min. The UV detector wavelength was 214 nm.

The HPLC–MS interface was a Hewlett-Packard direct liquid introduction (DLI) probe[11] (Hewlett-Packard, Palo Alto, CA, U.S.A.), which is a variable split-type interface with which only about 1% of the HPLC effluent enters the mass spectrometer ion source.

The mass spectrometer was a home-built 90°, 4-in. radius magnetic sector instrument equipped with a high-speed differential pumping system.

The LC–MS interface probe slides into a heated desolvation chamber made of MACOR glass ceramic (Corning Glass Works, Corning, NY, U.S.A.). The droplets of the jet coming out from the LC–MS interface probe were vaporized in the desolvation chamber and the solvent–sample mixture entered the ion source where it was ionized, the solvent serving as chemical ionization (CI) reagent. The MACOR desolvation chamber also served as electrical insulation between the ion source, which was at 1500 V, and the interface probe, which was at ground potential. Although a cold finger, cooled by liquid nitrogen, was mounted to provide additional cryogenic pumping, it was found that the system could also be operated without the cold finger[12].

Samples and solvents

Samples of explosives (pure compounds and technical mixtures) were obtained from the Israeli Police Analytical Laboratory. Standard samples and technical mixtures were dissolved in UV-grade acetone (Fluka, Buchs, Switzerland) or in UV-grade methanol (Fluka). The solvents used were UV-grade methanol and acetonitrile (Fluka) and triply distilled water. The solvents were filtered through a 1.0-μm filter (Whatman, Maidstone, U.K.) and sample solutions were filtered through a 0.5 μm filter (Millipore, Bedford, MA, U.S.A.).

RESULTS AND DISCUSSION

The compounds studied included the pure compounds nitroglycerin (NG), diethylene glycol dinitrate (DEGN), 2,4,6-trinitrotoluene (TNT) and 2,4,6-N-tetra-

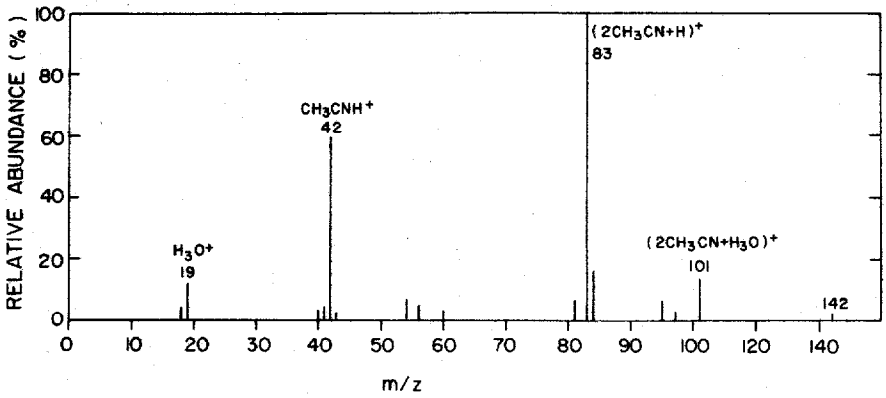


Fig. 1. High-pressure mass spectrum of acetonitrile–water (1:1).

nitro-N-methylaniline (tetryl) and technical mixtures including TNT, 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), pentaerythritol tetranitrat (PETN), NG and ammonium nitrate.

Mobile phase considerations

When using the direct liquid introduction interface, large amounts of solvent (serving as CI reagent) are introduced into the ion source of the mass spectrometer. Solvent peaks in the mass spectrum can interfere with sample peaks, and therefore the exact mass spectra of the solvents have to be known. Figs. 1 and 2 show the high-pressure mass spectra of acetonitrile–water (1:1) and methanol–water (1:1), respectively. Part of the mass spectrum in Fig. 2 has been scaled up in order to demonstrate the possibility of solvent peaks interfering with sample peaks which are in the same mass range.

The choice between methanol–water and acetonitrile–water as the mobile phase was governed by chromatographic separation considerations and by mass spectrometric performance. With regard to their performance as CI reagents, although having different reagent ions[13], no major difference was observed between the two solvents. However, voltage breakdowns between the ion source and the interface probe occurred more frequently with methanol than with acetonitrile.

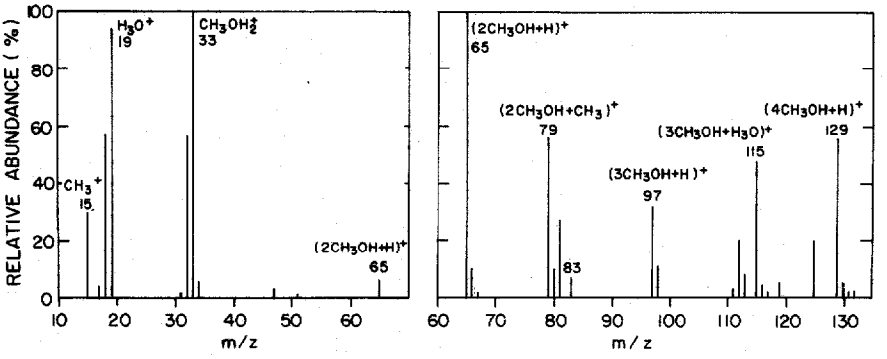


Fig. 2. High-pressure mass spectrum of methanol–water (1:1).

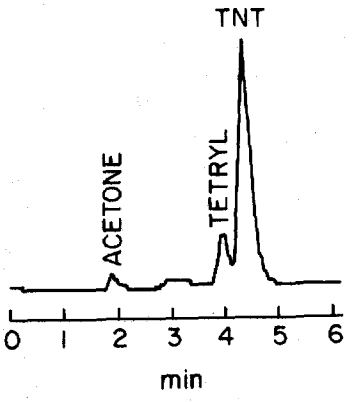


Fig. 3. HPLC–UV trace of a standard mixture of TNT and tetryl.

HPLC–UV traces and mass spectra

Fig. 3 shows the HPLC–UV trace of a standard mixture of TNT and tetryl using methanol–water (1:1) as the mobile phase. Figs. 4 and 5 show the respective LC–MS spectra of TNT and tetryl. The mass spectrum of TNT was characterized by the MH^+ ion at m/z 228, the adduct ion $(M + CH_3OH + H)^+$ at m/z 260, the

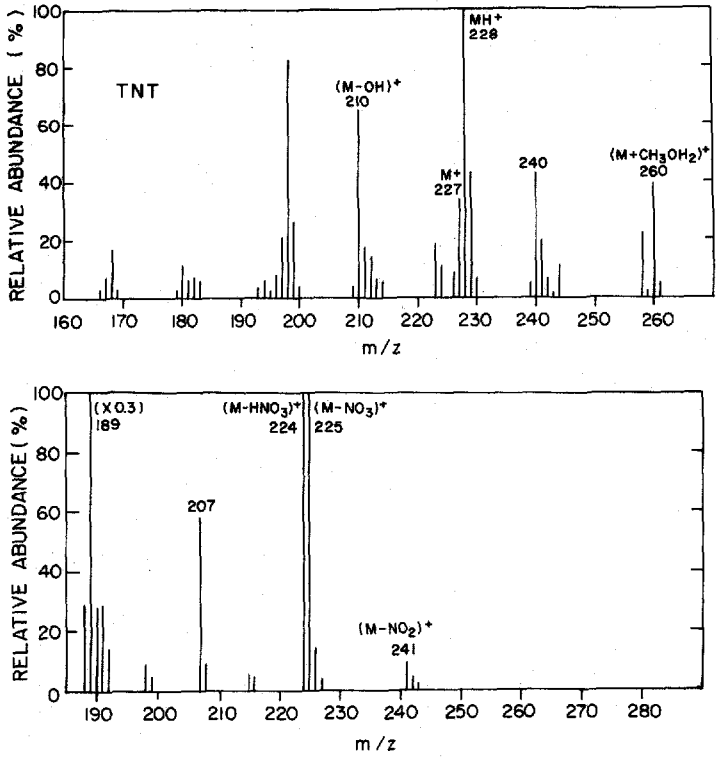
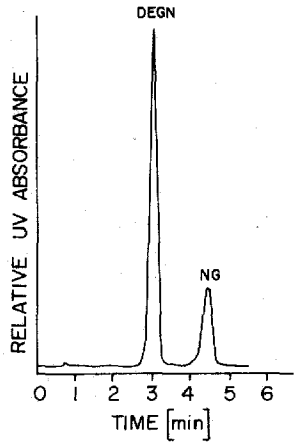


Fig. 4. LC–MS mass spectrum of TNT with methanol–water (1:1) as reagent.

Fig. 5. LC–MS mass spectrum of tetryl with methanol–water (1:1) as reagent.



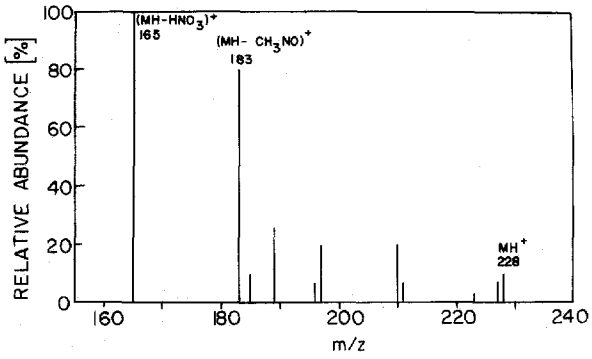
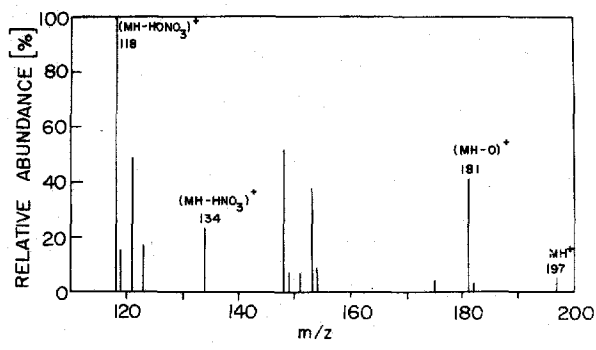


Fig. 6. HPLC–UV trace of a standard mixture of NG and DEGN.

Fig. 7. LC–MS mass spectrum of NG with methanol–water (1:1) as reagent.

molecular ion M^+ at m/z 227 and the fragment ions $(M - OH)^+$ at m/z 210, which is a typical electron impact (EI) ion, and the ion $(MH - 30)^+$ at m/z 198. This last ion is mainly due to a reduction process to the corresponding amine[14] and partly to loss of NO from the MH^+ ion. The mass spectrum of tetryl was characterized by typical[5] fragment ions: $(M - NO_2)^+$ at m/z 241, $(M - NO_3)^+$ at m/z 225 and $(M - HNO_3)^+$ at m/z 224. Although the HPLC separation of TNT and tetryl was not perfect, each of the separated components could be easily identified by its mass spectrum; it was therefore not necessary to find better HPLC separation conditions.

Fig. 6. shows the HPLC–UV trace of a standard mixture of NG and DEGN using methanol–water (1:1) as the mobile phase. Figs. 7 and 8 show the LC–MS mass spectra of NG and DEGN, respectively. The mass spectrum of NG was characterized by a small MH^+ ion at m/z 228 and typical[5] fragment ions $(MH - CH_3NO)^+$ at m/z



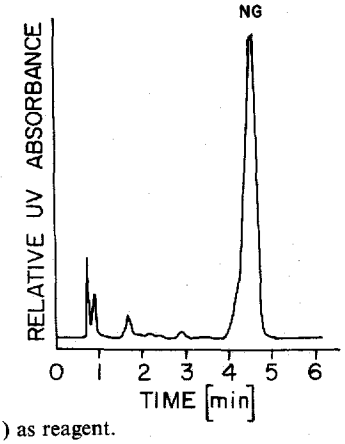


Fig. 8. LC–MS mass spectrum of DEGN with methanol–water (1:1) as reagent.

Fig. 9. HPLC–UV trace of a dynamite sample.

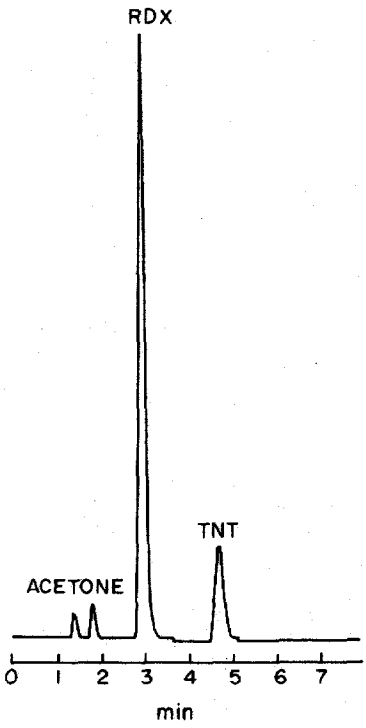


Fig. 10. HPLC–UV trace of a technical mixture containing TNT and RDX.

183 and $(MH - HNO_3)^+$ at m/z 165. The mass spectrum of DEGN was characterized by a small MH^+ ion at m/z 197 and by several fragment ions: $(MH - O)^+$ at m/z 181, $(MH - HNO_3)^+$ at m/z 134 and $(MH - HONO_3)^+$ at m/z 118.

Fig. 9 shows the HPLC–UV trace of a dynamite sample using methanol–water (1:1) as the mobile phase. The LC–MS mass spectrum of NG was similar to that in Fig. 7.

Fig. 10 shows the HPLC–UV trace of a technical mixture containing TNT and RDX with acetonitrile–water (1:1) as the mobile phase. Figs. 11 and 12 show the LC–

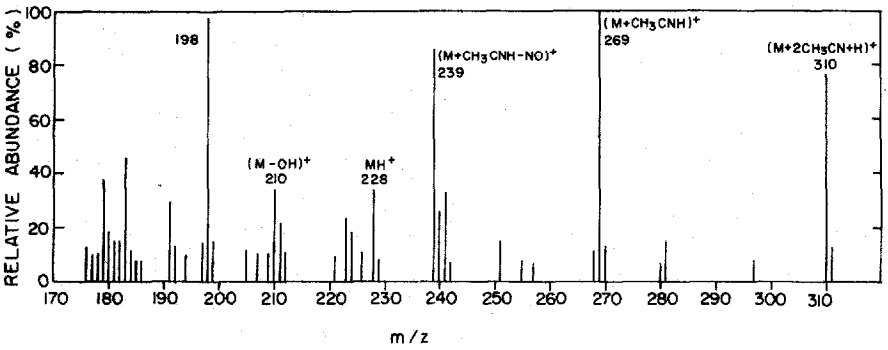


Fig. 11. LC–MS mass spectrum of TNT with acetonitrile–water (1:1) as reagent.

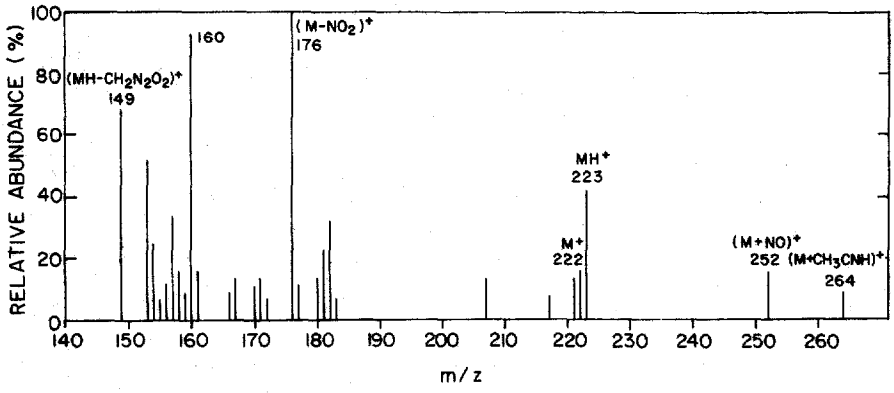


Fig. 12. LC–MS mass spectrum of RDX with acetonitrile–water (1:1) as reagent.

MS mass spectra of TNT and RDX, respectively. The mass spectrum of TNT was characterized by the MH^+ ion at m/z 228 and the fragment ions $(M - OH)^+$ at m/z 210 and $(MH - 30)^+$ at m/z 198 as in Fig. 4 and adduct ions, typical of the reagent, $(M + CH_3CN + H)^+$ at m/z 269 and $(M + 2CH_3CN + H)^+$ at m/z 310. The mass spectrum of RDX was characterized by the MH^+ ion at m/z 223, the M^+ ion at m/z 222, the adduct ions $(M + NO)^+$ at 252 and $(M + CH_3CN + H)^+$ at m/z 264 and typical[5] fragment ions $(M - NO_2)^+$ at m/z 176 and $(MH - CH_2N_2O_2)^+$ at m/z 149.

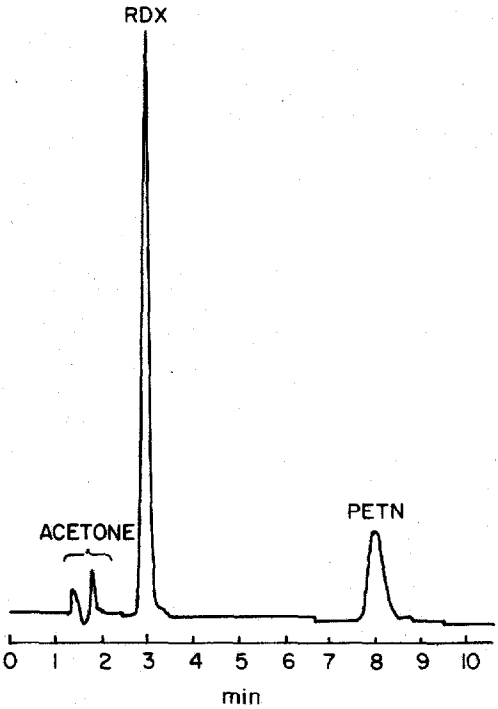


Fig. 13. HPLC–UV trace of a technical mixture containing RDX and PETN.

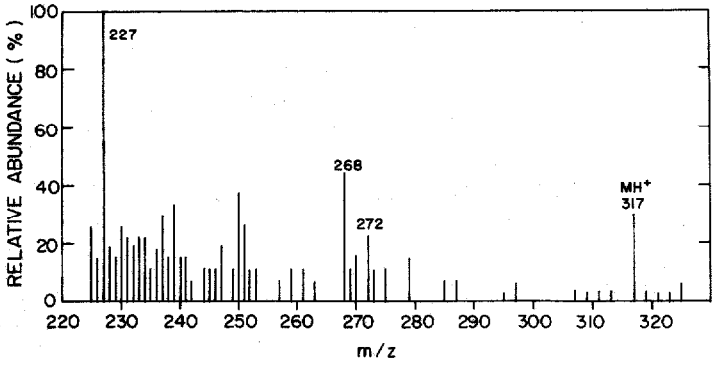
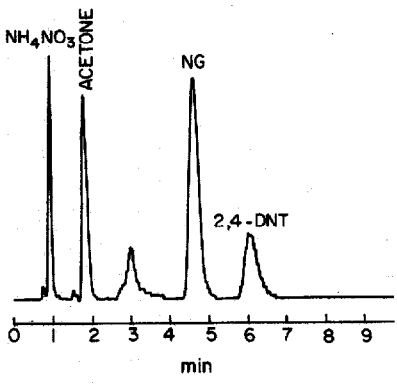


Fig. 14. LC–MS mass spectrum of PETN with acetonitrile–water (1:1) as reagent.

Fig. 13 shows the HPLC–UV trace of a technical mixture containing RDX and PETN, using acetonitrile–water (1:1) as the mobile phase. The LC–MS mass spectrum of RDX was similar to that in Fig. 12. Fig. 14 shows the LC–MS mass spectrum of PETN which contained the MH^+ ion at m/z 317 and many fragment ions.

Fig. 15 shows the HPLC–UV trace of a technical mixture containing NG, 2,4-DNT and ammonium nitrate, using methanol–water (1:1) as the mobile phase. With acetonitrile–water as the mobile phase it was difficult to separate 2,4-DNT and NG. The LC–MS mass spectrum of NG was similar to that in Fig. 7. Fig. 16 shows the LC–MS mass spectrum of 2,4-DNT which included mainly the following ions: $(M + CH_3CN + H - NO)^+$ at m/z 194, $(M + CH_3CN + H - 2NO)^+$ at m/z 164 and $(MH - 30)^+$ at m/z 153. No MH^+ ion was observed. The mass spectrum of ammonium nitrate could not be identified because of the difficulty in obtaining the mass spectrum of a salt and also because if any ions had been produced they would have been in the same mass range as the solvent ions.



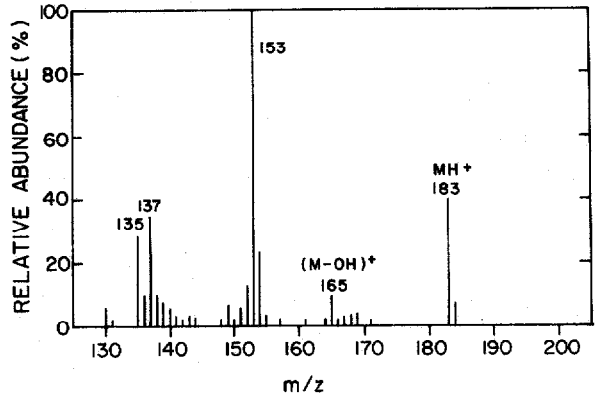


Fig. 15. HPLC–UV trace of a technical mixture containing NG, 2,4-DNT and ammonium nitrate.

Fig. 16. LC–MS mass spectrum of 2,4-DNT with methanol–water (1:1) as reagent.

CONCLUSIONS

The performance of the system was found to be optimal when the ion source of the mass spectrometer was not entirely closed, so that the local pressure in the ion source was not too high. This was achieved by having an opening in the ion source or by keeping the DLI probe a few millimetres from the desolvation chamber.

In the direct liquid introduction method, because only 1 % of the effluent enters the mass spectrometer, about 2 orders of magnitude of sensitivity are lost. In order to obtain identifiable mass spectra, sample amounts of 1–10 μg were injected into the HPLC system (*ca.* 10–100 ng in the ion source). These amounts can be considerably reduced by using integration techniques or single ion monitoring.

In summary, LC–MS with the DLI interface is a promising method for the analysis of explosives; the HPLC provides efficient separation of explosive mixtures while the mass spectrometer identifies, by chemical ionization, the various separated components by means of their MH^+ and/or characteristic adduct and fragment ions.

ACKNOWLEDGEMENT

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