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Chromatographic and Spectrometric Identification of Propyl Isopropylphosphonofluoridate and its Degradation Products

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Abstract: The study demonstrates how Gas Chromatography/Mass Spectrometry (GC/MS) and Liquid Chromatography/Mass Spectrometry (LC/MS) techniques are applied for identification of sarin type of nerve agents. A brief historical review of Chemical Weapon Convention (CWC) has been presented. GC/MS and LC/MS as analytical techniques have been used for the identification of Propyl isopropylphosphonofluoridate and its degradation products. While the Propyl isopropylphosphonofluoridate was identified with the GC/MS, its degradation products were identified with LC/MS. Analysis of the propyl isopropylphosphonofluoridate with the GC/MS produced a mass spectrum with a base ion with charge to mass ratio of 127. The mass spectrum of propyl isopropylphosphonate using LC/MS produced a deprotonated molecular ion at mass to charge ratio of 165, while a similar spectrum of isopropylphosphonic acid produced a deprotonated molecular ion with mass to charge ratio of 123.

Key words: Chemical weapon convention, fragmentation, ionization, molecular ion, nerve agents, spectrum

INTRODUCTION

Propyl isopropylphosphonofluoridate is a chemical warfare agent and a listed chemical of the Chemical Weapon Convention (CWC). As a result of this the chemical weapon convention prohibits the development, production, stockpiling and the use of this chemical. The chemical weapon convention which entered into force on 29th April 1997 (Kientz, 1998) prohibits development, production, stockpiling and the use of chemical weapons. At the moment 182 countries have signed the convention and all member states are obliged to abide by the provisions of the convention. Organization for Prohibition of Chemical Weapons (OPCW), an International Organization in The Hague, Netherlands, is the convention implementing body.

Chemical warfare agents can be divided into several groups and the most lethal group is the nerve agents. The name nerve agent is derived from the action of these chemicals on the nervous system. The nerve agents irreversibly react with the enzyme acetyl cholinesterase in the tissue fluid that results in the accumulation of acetylcholine and continuous stimulation of the nervous system. One nerve chemical sarin, which is isopropyl methylphosphonofluoridate, was used in 1988 against the Kurdish village of Birjinni. In 1994 and 1995, terrorist attacks in Matsumoto and the Tokyo underground system used sarin. Even though the terrorists used impure sarin and primitive delivery system, it was effective to kill 12 people and injured more than 5000 others (Hooijschuur *et al.*, 2002).

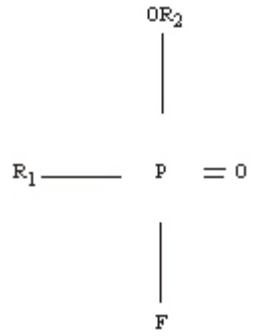

Fig. 1: General structural formula for sarin type of nerve agents

It is against this background that the use of sarin and related chemicals such as propyl isopropylphosphonofluoridate are banned under the CWC. Sarin and related chemicals, which are banned under the CWC, form a homologous series with general formula as indicated in Fig. 1.

$R_1 = C_1$-C_3 [methyl, ethyl and propyl (normal or isopropyl)], $R_2 = C_1$-C_{10} [methyl, ethyl, propyl… decayl], cyclic groups [cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl… cylcodecayl] are also included. Compounds whose structural formulae could be derived from the above general formula are toxic and are referred to as sarin type of nerve agent. They form the schedule I .A .I of the chemical weapon convention annex on chemicals (Mesilaakso and Rautio, 2000). It must be indicated clearly that the use of precursors and degradation products of these nerve agents is also prohibited under the CWC.

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Propyl isopropylphosphonofluoridate has R_1 as isopropyl and R_2 as n-propyl. In the present of water, propyl isopropylphosphonofluoridate undergoes degradation to form two main products. These are propyl isopropylphosphonate and isopropylphosphonic acid. These two chemicals are all relevant to the CWC. They are therefore listed as schedule chemicals and their schedule number is 2. B. 4 (Annex on Chemical of CWC, 1997).

Verification of CWC requires development of reliable and validated analytical methods for trace level analysis of chemical warfare agents (Soderstrom and Ketola, 1994). Chromatographic and spectrometric techniques such as Gas Chromatography/Mass Spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), Gas Chromatography/Fourier Transformed Infrared Spectrometry (GC/FTIR) and Nuclear Magnetic Resonance spectrometry (NMR) have been used for the study of chemical warfare agents in water, soil, air and polymetric materials (Mesilaakso, 1998). In the review of derivatization reactions in the chromatographic analysis of chemical warfare agents and their degradation products Robin and Bob emphasized GC/MS and LC/MS among others as some of the analytical separation techniques for the determination of chemical warfare agents (Robin and Bob, 2003). The use of gas chromatography equipped with nitrogen-phosphorus detector, though could be sufficient for identification of sarin type of nerve agent, for unambiguous identification, OPCW requires that such analysis must be confirmed with techniques such as GC/MS, GC/FTIR and NMR. It has reported that most degradation products of sarin type of nerve agent are polar in character and therefore LC/MS is most suitable for the identification of such products (Noort *et al*., 1997)

In this study propyl isopropylphosphonofluoridate prepared in ethyl acetate and in water/methanol were analyzed and identified using GC/MS and LC/MS techniques.

MATERIALS AND METHODS

This study was conducted in December 2006 at the Finish Institute for Verification of Chemical Weapon Convention (VERIFIN) in Helsinki, Finland.

Chemicals and samples: The chemicals and samples used for the investigation were supplied by VERIFIN. Two samples, organic and water samples of propyl isopropylphosphonofluoridate were used for the investigation. The samples were already in an aliquot form, each in 2 mL vial and they were used without further treatment. The organic sample of propyl isopropylphosphonofluoridate was prepared in ethyl acetate while the water sample was prepared in 1:1 methanol/water.

Gas Chromatography/Mass Spectrometry (GC/MS): The GC/MS were Perkins Elmer, TurboMass Gold and VG Auto SpecQ Spectrometers. The former was used for the Electron Ionization (EI) analysis while the latter was used for the Chemical Ionization (CI) investigation. In both cases splitless injections were done and the splitless time was 1 minute. The injector temperature was 250ºC . The Column for the two instruments was SE-54 brand with dimension; 28 m x 0.25 mm x 0.25 µm. GC temperature programme was 40ºC (1min), 10ºC/min, 280ºC (10 min). Typical electron energy of 70 eV was applied for the EI while in the case of the CI experiment ammonia was used as the reagent gas. The scan range was 30-500 m/z with a scan time of 0.2 sec. The organic sample was analyzed with these techniques.

Liquid Chromatography/Mass Spectrometry (LC/MS): The LC/MS was a Micromass Quattro II Mass Spectrometer with atmospheric pressure chemical ionization (APCI) probe interface. It is equipped with HP 1100 LC binary pump, HP LC auto sampler, HP 1100 LC control module. The column was C-18 Water Bridge™ with dimension 1.0 x 100 mm and particle size of 5.0 µm. Flow speed 1ml/min, Injection volume 5 µL. Eluents 20 mMol NH_4Ac, pH(8.5)A and MeOH(B), Gradient 5%B → 100%B/5 min + 20 min isocratic. The water sample was analysed with this technique.

RESULTS AND DISCUSSION

Figure 2 is the total ion chromatograph (TIC) for the GC/MS analysis of the organic sample of propyl isopropylphosphonofluoridate using electron ionization showing the chemical, propyl isopropylphosphonofluoridate eluting at 7.01 min, while Fig. 3 is its corresponding Extraction Ion Chromatograph (EIC) obtained by taken a spectrum from the TIC. The Extraction Ion Chromatograph (EIC) of the chemical (Fig. 3) is the mass spectrum of propyl isopropylphosphonofluoridate. The base peak with mass to charge ratio of 127 is typical of the mass spectrum of sarin type of nerve agents where R_1 (Fig. 1) is a propyl group (Standardization of Techniques and Reference Data, 1999). The base ion is formed as a result of lost of C_3H_5 radical from propyl isopropylphosphonofluoridate. The peaks with mass to charge ratio of 111, 125, 139 and 153 are formed as a result of lost of C_3H_5O, C_3H_7, C_2H_5 and CH_3 respectively. A critical feature in the spectrum, which indicates that R_2 is n-propyl and not isopropyl is the intensity of $[M\text{-}CH_3]^+$ ion (m/z 153). Its low abundance means that the CH_3 was lost from n-propyl and not from the isopropyl group as fragmentation of CH_3 from isopropyl group always produces and an intense $[M\text{-}CH_3]^+$ ion (Kientz, 1998).

Spectrum obtained when the organic sample was analyzed with the GC/MS using chemical ionization is

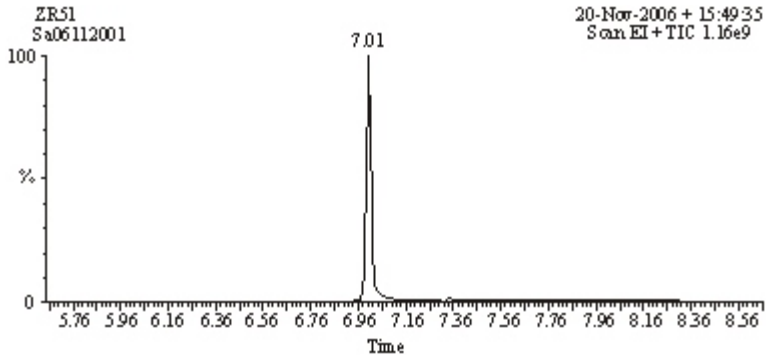


Fig. 2: Total ion chromatograph (TIC) of propyl isopropylphosphonofluoridate recorded with Perkins Elmer Turbo Mass Gold GC/MS by running Electron Ionization (EI) experiment

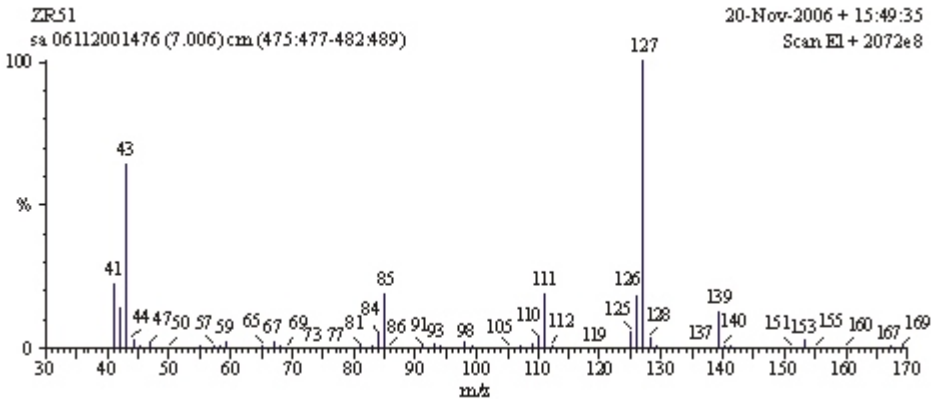


Fig. 3: EI mass spectrum of propyl isopropylphosphonofluoridate on Perkins Elmer. Turbo Mass Gold GC/MS

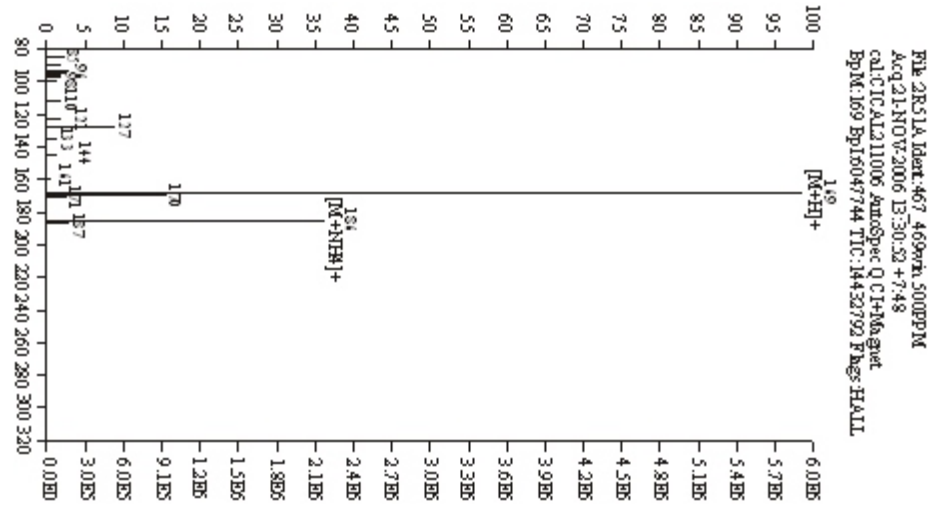


Fig. 4: Mass spectrum of Propyl isopropylphosphonofluoridate recorded with VG Auto SpecQ Spectrometer by running ammonia Chemical Ionization (CI)

presented in Fig. 4. The most prominent peak at mass to charge (m/z) ratio of 169 is the protonated molecular ion peak $[M+H]^+$. It can therefore be inferred that the molecular weight of the compound is 168, which confirms propyl isopropylphosphonofluoridate. The peak at 186 is the peak for it ammonium adduct $[M+NH_4]^+$ which often characterized ammonia gas chemical ionization mass spectrum (Munson, 2000). The mass of the ammonium adduct of 186, also confirms the molecular weight of 168 for the chemical.

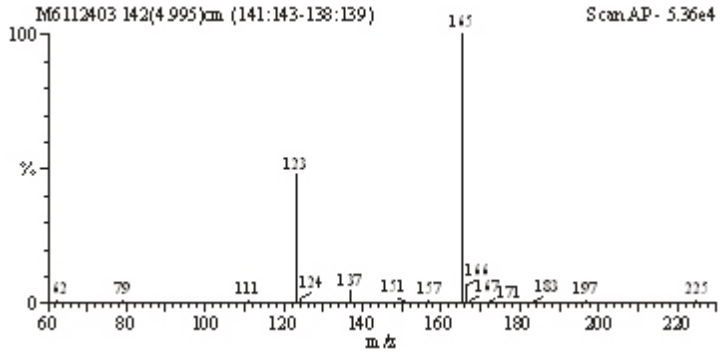


Fig. 5: LC/MS mass spectrum of propyl isopropylphosphonate recorded with micromass quattro II mass spectrometer using APCI-

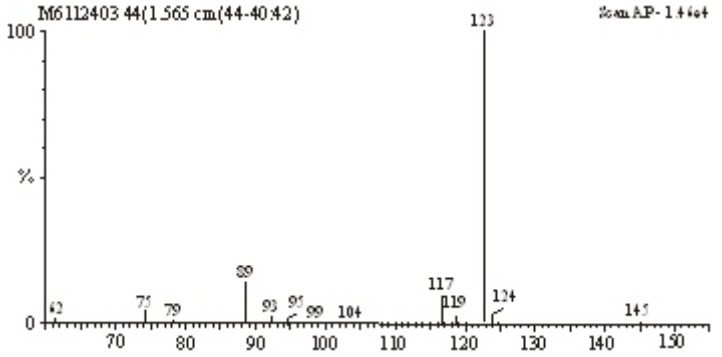
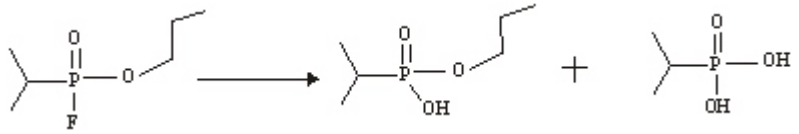


Fig. 6: LC/MS mass spectrum of isopropylphoshonic acid, recorded with Micromass Quattro II Mass Spectrometer using APCI-



propyl isopropylphosphonate isopropylphosphonic acid

Fig. 7: Degradation pathway of propyl isopropylphosphonofluoridate

Results of the LC/MS spectra of the water sample of propyl isopropylphosphonofluoridate are presented in figures 5 and 6. In an environment of water, propyl isopropylphosphonofluoridate readily undergoes hydrolysis to produce propyl isopropylphosphonate and isopropylphosphonic (Soderstrom and Ketola, 1994). The degradation pathway of propyl isopropylphosphonofluoridate is as shown in Fig. 7.

Figure 5 is the mass spectrum of propyl isopropylphosphonate and the most prominent peak at 165 is the deprotonated molecular ion peak $[M-H]^-$ which means the molecular weight of the chemical is 166 confirming propyl isopropylphosphonate. Figure 6 is the mass spectrum of isopropylphosphonic acid. The base peak with mass to charge ratio of 123 is the deprotonated molecular ion $[M-H]^-$ peak, which means a molecular weight of 124 for the compound and confirms isopropylphosphonic acid.

CONCLUSION

Propyl isopropylphosphonofluoridate can unambiguously be identified with GC/MS by running both electron and chemical ionization experiments. The electron ionization spectrum of the chemical produced a base peak with mass to charge ratio of 127, while the chemical ionization spectrum produced a protonated molecular ion with mass to charge ratio of 169. The degradation products, propyl isopropylphosphonofluoridate and isopropylphosphonic acid were also identified with LC/MS using atmospheric pressure chemical ionization in the negative mode. The mass spectrum obtained for propyl isopropylphosphonate produced a deprotonated molecular ion with mass to charge ratio of 165, while that of isopropylphosphonic acid has its deprotonated molecular ion at 123.

ACKNOWLEDGMENT

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