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On-matrix derivatisation–extraction of precursors of nitrogen- and sulfur-mustards for verification of chemical weapons convention

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Abstract

Development and refinement of sample preparation protocols for retrospective detection and identification of chemical warfare agents (CWAs) and their markers is of paramount importance from verification point of view of chemical weapons convention (CWC). Precursors of nitrogen- and sulfur-mustards (NMPs and SMPs) are polar adsorptive markers of vesicant class of CWAs. Their detection in a given environmental sample may imply past contamination with mustards. For the efficient extraction of NMPs and SMPs from soil, on-matrix derivatisation–extraction (OMDEX) method was developed and optimized. The method involved trifluoroacetylation of analytes on soil itself, followed by extraction with suitable solvent. The extracted samples were analyzed by gas chromatography–mass spectrometry (GC–MS). This virtually single-step sample preparation offered better recoveries of NMPs and SMPs in comparison to conventionally used extraction, evaporation and derivatisation. The best recoveries of analytes were obtained with acetonitrile by OMDEX method. Dynamic linearity range of trifluoroacetylated (TFA) derivatives of NMPs and SMPs was 1–12 μg/L in GC–MS analysis in SIM mode. Repeatability and reproducibility of this technique containing 5 and 10 μg analytes/gm soil was <3.3% and <4.6%, respectively. OMDEX technique was finally applied for the detection of TFA derivatives of NMPs in the soil sample supplied in 16th official proficiency test conducted by OPCW in October 2004.

Keywords: Nitrogen mustard; Sulfur mustard; Chemical weapons convention; Verification; Derivatisation; Extraction

1. Introduction

The development of efficient analytical procedures for chemical warfare agents (CWAs) and their characteristic degradation compounds is an important area of contemporary research [1–5]. The methods aiming for extraction, detection and identification of CWAs and related compounds are crucial (i) to identify and monitor cleanup of contaminated area and (ii) to verify the compliance or non-compliance of chemical weapons convention (CWC). The CWC came in existence in April 1997 with the objective of prohibition on proliferation of CWAs [6,7]. The treaty is administered by the Organization for Prohibition of Chemical Weapons (OPCW), through its strict verification regime [6–8]. Verification involves inspection of declared and suspected chemical weapons (CW) facilities. Environmental samples such as soil, water, vegetation etc are collected from these facilities and subjected to unequivocal identification of convention-related compounds (CRCs), which includes CWAs, their analogues, precursors and characteristic degradation compounds (so called signatures/markers). The CRCs are included in three schedules of CWC based on their potential risk to the convention [6,7].

The analysis of collected samples is generally performed on-site by the inspectors. In case of any ambiguity, the samples are sent to designated laboratories appointed by the OPCW for unequivocal identification of CRCs [8–12]. The OPCW maintains a network of designated laboratories by periodically evaluating their analytical capabilities through official proficiency tests (OPTs) [9–11].

The analytical procedure of CRCs in environmental matrices involves four major steps: (i) extraction (ii) concentration (iii) derivatisation and (iv) identification [12]. First three

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steps are collectively called sample preparation, for which recommended operating procedures (ROPs) have been devised and updated based on results of official proficiency tests [12,13]. The sample preparation methods are directed to produce liquid extracts that are subsequently subjected to identification of CRCs. According to the OPCW rules, the identification of CRCs must be carried out by a combination of two spectrometric techniques or one plus one GC retention index [11]. Gas chromatography coupled to mass spectrometry (GC–MS) is the most preferred technique due to its wide range application and the existence of huge data base [14,15].

Amongst various environmental matrices, soil is the most likely matrix to be contaminated in any deliberate or inadvertent spread of CWAs. Hence, detection and identification of CRCs in soil is of prime importance from verification point of view of CWC. Analysis of polar CRCs are reported involving various techniques such as reverse-phase microcolumn liquid chromatography coupled to flame photometric and electrospray ionization mass spectrometry [16], GC–MS after extraction [17], supercritical fluid extraction [18], liquid chromatography–mass spectrometry [19] and capillary electrophoresis [20]. Still the search of efficient extraction procedures of CWAs and their markers/signatures from soil and other matrix is continuing [21–24].

As per ROPs, the extraction of polar CRCs from soil is performed with methanol, methanol containing triethylamine and water, which are evaporated in subsequent step prior to derivatisation as protic solvents hamper the derivatisation reaction (trimethylsilylation or trifluoroacetylation) [12,13,25,26]. Evaporation of solvents causes loss of analytes (depending on their volatility) to some extent and moreover the extractions, concentration followed by derivatisation are also time-consuming processes. Keeping these constraints in view, we thought that if polar CRCs are converted into their non-polar derivatives on soil itself, and then extracted with suitable solvent, their recoveries would probably be enhanced. Because, the polar functions responsible for the strong adsorption will get masked by derivatisation reaction, and the extraction of derivatised analytes in subsequent step can be realized effectively with organic solvents. Thus the derivatisation and extraction can virtually be performed in a single step, with elimination of evaporation process. Somewhat reverse of this intended technique is reported with carboxylic acids and phosphonic acids, where extraction followed by derivatisation (extractive-alkylation) is performed on soil and bio-fluids [22,23,27,28]. But to the best of our information, no quantitative on-matrix derivatisation–extraction (OMDEX) of polar CRCs like precursors of nitrogen- and sulfur-mustards, is reported. It prompted us to study the recoveries of precursors of nitrogen- and sulfur-mustards from soil by derivatisation–extraction method, and compare with those obtained with routine sample preparation methods given in ROPs. These compounds were selected because owing to amine and hydroxyl functions they are likely to be strongly adsorbed on soil.

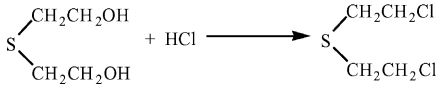

Fig. 1. Formation of sulfur-mustard from SMP1.

Nitrogen- and sulfur-mustards (NMs and SMs) are cytotoxic, alkylating and blistering agents and are respectively placed in schedule 1.A.4 and 1.A.6 of CWC [6,7]. Precursors of NMs (schedule 3.B.15/16/17) and SMs (schedule 2.B.13, the thiodiglycol only) are ethanolamines and 2-hydroxy ethyl (thio)ethers, respectively, which produce corresponding mustards in a single step by nucleophilic substitution of hydroxyl group by chlorine, as typically illustrated in Fig. 1. Moreover, the same compounds are also produced by hydrolytic degradation of corresponding mustards. Hence, these precursors of nitrogen-mustards (NMPs) and sulfur-mustards (SMPs) function as important markers of respective class of vesicants. Their identification in a sample submitted for analysis may imply past contamination with mustards.

Recently, we have reported a fast and convenient trifluoroacetylation (derivatisation) of NMPs and SMPs with *N*-trifluoroacetylimidazole (TFAI) and *N*-trifluoroacetylbenzimidazole (TFABI) [29]. Trifluoroacetylations of NMPs and SMPs are advantageous over conventional trimethylsilylations in terms of selectivity, sensitivity, efficiency and less background in total ion chromatogram. For the present investigation, the same trifluoroacetylation reactions were adopted for on-matrix derivatisation–extraction of NMPs and SMPs from soil. Representative examples of NMPs and SMPs selected for the study are shown in Fig. 2.

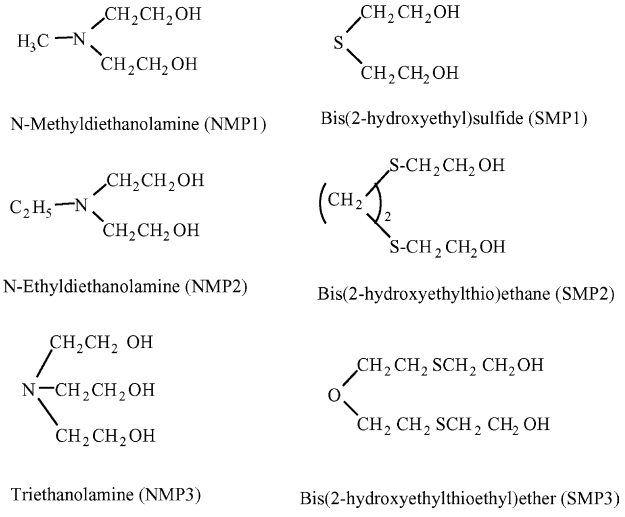

Fig. 2. Precursors of nitrogen- and sulfur-mustards.

2. Experimental

2.1. Reagents and chemicals

Organic solvents (analytical grade) toluene, heptane, hexane, dichloromethane, ethyl acetate, chloroform, acetonitrile, and butanone were obtained from Aldrich Chemical Co. USA and were used as received. *N*-Trifluoroacetylimidazole, pentadecane, *N*-methyldiethanolamine, *N*-ethyldiethanolamine, triethanolamine and bis(2-hydroxyethyl)sulfide were obtained from Fluka (Sigma–Aldrich, Powai, Mumbai, India). Other precursors (SMP2 and SMP3) were synthesized as per reported procedure [30], and were determined to be >96% pure by GC–MS analysis.

2.2. Soil

Local soil (sand) collected from the vicinity of our laboratory was free of organic matter and silt. Its water suspension showed the pH of 6.8. It was sieved (2 mm) and dried for two days at 60 °C before spiking.

2.3. Standard and spiking solutions

Stock standard solutions of analytes (1 g/L) were prepared in chloroform separately by accurately weighing ~0.01 g of analyte into 10 mL volumetric flask and diluting to volume. From these solutions, intermediary standard solutions of 200 μg/mL were prepared by diluting with chloroform. Aliquots (500 μL) of each of these intermediary standards were treated with 100 μL of TFAI and the volume was finally adjusted to 2.0 mL with *n*-heptane. It gave the working standard solution of 50 μg/mL of each of derivatised analytes. Stock standard solution of internal standard pentadecane was prepared in similar way at the concentration of 1 g/L in *n*-heptane. An intermediary standard of 100 mg/L was prepared from this by diluting 10 times with *n*-heptane. A series of working standard solutions was prepared by serial dilution of '50 μg/mL working standard' of derivatised analytes with *n*-heptane to fulfill the requirements for the construction of calibration curve. For this, 100 μL of intermediary standard (100 mg/L) of internal standard plus 40, 80, 160, 320 and 480 μL of derivatised working standard (50 μg/L) were mixed serially and the volumes of all the final working standards were adjusted to 2.0 mL with *n*-heptane. It gave the serial concentration of derivatised analytes from 1 to 12 μg/mL with fixed concentration (5 μg/mL) of internal standard.

2.4. Spiking of soil

For spiking, a working standard solution of NMPs and SMPs was prepared at the concentration of 20 μg/mL of each analyte in dichloromethane. It was prepared by taking 500 μL from intermediary standard solutions (200 μg/mL) of each analyte and adjusting the final volume to 5.0 mL with dichloromethane. Soil (10 g) was weighed into a 25 mL screw capped glass bottle and spiked with 5.0 mL this working standard solution containing all the analytes, it gave the spiking level of 10 μg/g. Spiked soil was allowed to stand overnight in screw capped bottle to adsorb the analytes, and then the solvent was evaporated at ambient temperature under the gentle stream of nitrogen. The dried soil was tightly closed until the experimentation.

2.5. Derivatisation–extraction procedure

Derivatisation combined with extraction was performed with variety of solvents to get the best possible recovery. A typical procedure is described as follows. Spiked soil (500 mg) was taken in a 2.0 mL teflon capped vial and treated with 250 μL of *N*-trifluoroacetylimidazole by gently shaking for 5 min. It was subsequently extracted with 3 × 150 μL acetonitrile by shaking for 2 min. Acetonitrile extracts were separated, combined and mixed with 50 μL of internal standard pentadecane (100 mg/L) and final volume was adjusted to 1 mL with acetonitrile before subjecting it to GC–MS analysis. Soil (sandy) sample supplied by OPCW in 16th proficiency test was also subjected to derivatisation–extraction in similar way. This test was conducted in the month of October 2004, and the soil fortified with all the three precursors (NMPs) of nitrogen-mustards was given for their unambiguous identification.

2.6. Conventional extraction

Extraction, concentration and derivatisation of spiked soil was performed as per ROPs. In three different experiments, soil (500 mg) was extracted with 3 × 300 μL of solvents: methanol, methanol containing 1% triethylamine and water, by vigorous shaking. Extracts were combined after centrifugation and evaporated to almost dryness under stream of nitrogen or rotary evaporator. Residue was reconstituted in 250 μL acetonitrile followed by addition of 250 μL TFAI and 50 μL internal standard (100 mg/mL). Final volume was adjusted to 1 mL with acetonitrile.

2.7. GC–MS analysis

The GC–MS analyses were performed in electron ionization (EI) (70 eV) in selected ion monitoring (SIM) mode with an Agilent 6890 GC equipped with a model 5973 mass selective detector (Agilent technologies, USA). An SGE BPX5 capillary column with 30 m length × 0.32 mm i.d. × 0.25 μm film thickness was used at temperature program of 80 °C (2 min)–5 °C/min–120 °C (0.5 min)–20 °C/min–280 °C (1.5 min). The retention time and ions selected to monitor the trifluoroacetylated (TFA) derivatives of NMPs and SMPs are given in Table 1. The complete description of EI mass spectra of these derivatives is already reported [29].

Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min. The samples were analyzed in splitless

Table 1
The retention time and ions selected to monitor the TFA derivatives of NMPs and SMPs

Entry	Analytes	Ions monitored (relative abundance)	Retention time (RT) (min)
1	TFANMP1	184, 198 (100), (9)	4.27
2	TFANMP2	198, 212 (100), (10)	5.40
3	TFANMP3	310, 324 (100), (16)	10.36
4	TFASMP1	141, 200 (91), (31)	6.39
5	TFASMP2	141, 201 (100), (50)	13.77
6	TFASMP3	141, 201 (100), (36)	15.28
7	Pentadecane (IS)	57, 71 (100), (65)	12.78

mode at injection temperature of 250 °C, EI source temperature 230 °C and quadrupole analyzer at 150 °C. The GC–MS analysis of proficiency test soil sample was performed in full scan mode at a temperature program of 45 °C (3 min)–8 °C/min–280 °C (5 min).

3. Results and discussion

3.1. Derivatisation and mass selective detection

Trifluoroacetylation reaction with triethanolamine (NMP3) and *N*-trifluoroacetylimidazole is typically illustrated in Fig. 3. Trifluoroacetylation reactions with TFAI are advantageous in comparison to commonly used trifluoroaceticanhydride, as they do not require a base to drive the reaction to completion. These reactions with NMPs and SMPs have already been optimized in terms of time, temperature, yields and solvent [29]. The reaction is completed within 5 min at room temperature in aprotic solvent. The trifluoroacetylation reactions for 'derivatisation–extractions' were performed on soil itself followed by extraction with various solvents.

Mass selective detection of trifluoroacetylated derivatives of NMPs (TFANMPs) and SMPs (TFASMPs) was performed by selected ion monitoring of two characteristic fragment ions in EIMS. TFANMPs characteristically produce $[M-113]^+$ (by loss of CF_3COO radical) and $[M-127]^+$ (by loss of CF_3COOCH_2 radical) fragment ions; latter fragmentation gives rise to the base peak. Hence both of these peaks were selected for detection of TFA derivatives in SIM mode. Similarly one of the fragment ions selected for detection of TFASMPs in SIM mode was responsible for generating the base peak; it was formed at *m/z* value of 141 by the species $[CF_3COOC_2H_4]^+$. The second ion selected for TFASMP1 was 200, formed by neutral loss of CF_3COOH from the molecular ion; and for TFASMP2 and TFASMP3, the second ion was 201 formed by the species $[C_2H_4SC_2H_4OCOCF_3]^+$. For the internal standard pentadecane, the ions selected in SIM mode were 57 and 71. The retention time of TFA derivatives of NMPs and SMPs along with the ions selected for analysis in SIM mode are given in Table 1.

3.2. Calibration plots

Before studying the quantitative recoveries of analytes by derivatisation–extraction from soil, the linearity of GC–MS analysis in SIM mode was ensured by running a series of standard solutions. Standard solutions of analytes were prepared in triplicate over the range of 1–12 μg/mL. The ratios of peak areas of analyte-to-internal standard were used for the construction of calibration plots and quantification. A summary of calibration plots is presented in Table 2. Satisfactory linearity was obtained for the employed GC–MS (SIM) method as demonstrated by correlation coefficients higher than 0.9980.

3.3. Selection of solvent for derivatisation–extraction

To achieve good extraction, solvents differing in polarity were screened. Initially, the derivatising agent TFAI was added on the spiked soil and left for 5 min to react with analytes. Subsequently the derivatised analytes were extracted with the solvent. The recoveries of trifluoroacetylated derivatives of NMPs and SMPs with different solvents are summarized in Table 3. The results are average of triplicate runs. The best recoveries of all the analytes were obtained with acetonitrile. It is note worthy that recoveries of TFA derivative of NMP3 were higher than that of NMP1 and NMP2 with almost all the solvents. This observation can be explained by better partitioning of TFANMP3 from soil into organic layer by virtue of its relatively higher hydrophobicity than that of TFANMP1 and TFANMP2. Higher hydrophobicity of TFANMP3 over TFANMP2 and TFANMP1 could be attributed to presence of an extra trifluoroacetyl group and more symmetric structure. In conventional sample

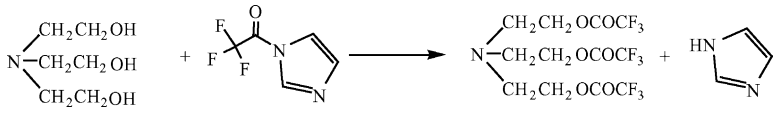

Fig. 3. Trifluoroacetylation of triethanolamine (NMP3) with TFAI.

Table 2
Analytical figures of calibration for TFA derivatives of NMPs and SMPs in GC–MS-SIM

Entry	Analytes	Calibration plot		r^2	DLR[a] (μg/mL)
		Slope	Intercept		
1	TFANMP1	0.0532 ± 0.0005	−0.0099 ± 0.0003	0.9982	1–12
2	TFANMP2	0.2006 ± 0.0009	0.0102 ± 0.0021	0.9987	1–12
3	TFANMP3	0.1688 ± 0.0007	−0.0071 ± 0.0002	0.9992	1–12
4	TFASMP1	0.1149 ± 0.0005	0.0086 ± 0.0004	0.9987	1–12
5	TFASMP2	0.1940 ± 0.0006	−0.0467 ± 0.0016	0.9994	1–12
6	TFASMP3	0.1936 ± 0.0011	−0.0829 ± 0.0005	0.9993	1–12

[a] Dynamic linearity range.

Table 3
Recoveries of NMPs and SMPs from fortified soil by OMDEX with various solvents

Entry	Solvent	Recovery (%)					
		NMP1	NMP2	NMP3	SMP1	SMP2	SMP3
1	Hexane	21.9 ± 2.1	22.7 ± 2.0	27.0 ± 1.8	20.9 ± 2.2	20.7 ± 1.9	20.1 ± 3.3
2	Carbon disulfide	21.8 ± 3.2	23.0 ± 3.4	28.9 ± 3.2	20.6 ± 3.6	21.8 ± 3.3	19.9 ± 3.8
3	Dichloromethane	25.3 ± 1.8	25.2 ± 2.0	46.4 ± 3.1	23.9 ± 2.3	22.8 ± 1.1	23.8 ± 2.1
4	Chloroform	23.0 ± 2.8	22.2 ± 3.1	39.1 ± 2.9	20.8 ± 3.0	21.3 ± 2.7	22.6 ± 2.4
5	Toluene	23.3 ± 2.1	25.0 ± 2.5	36.9 ± 2.3	21.2 ± 3.0	22.8 ± 1.7	24.7 ± 2.2
6	Ethylacetate	47.6 ± 3.2	47.2 ± 3.5	58.1 ± 3.4	52.3 ± 3.7	59.5 ± 3.1	46.6 ± 3.0
7	Butanone	54.6 ± 3.8	54.3 ± 3.1	71.8 ± 3.3	52.6 ± 3.7	59.9 ± 3.4	46.8 ± 2.8
8	Acetonitrile	79.0 ± 3.1	79.0 ± 3.6	88.6 ± 3.0	86.0 ± 3.7	85.3 ± 2.1	86.6 ± 3.3

preparation, the results were of reverse order, as shown in Table 4 (entry 1). Extraction with methanol resulted in inferior recovery of NMP3 in comparison to NMP2 and NMP1; it clearly demonstrates the strong adherence of triethanolamine on soil over NMP2 and NMP1 owing to presence of one extra hydroxyl group. This strong adsorption was wrecked when polar hydroxyl functions were masked by trifluoroacetylation and recovery of NMP3 was better with OMDEX technique.

Further, the recoveries of NMPs were lower than that that of SMPs in methanol by conventional method (entry 1, Table 4). Nitrogen of NMPs gets protonated on acidic surface of sand thereby hindering their extraction; whereas in water the recoveries of all the analytes were significantly enhanced (entry 2, Table 4).

With OMDEX technique, the recoveries of all the NMPs were better than even with water in conventional technique (entry 8, Table 1 and entry 2, Table 2). It should be noticed that otherwise poorly extractable NMP3 was best recovered (88%) in acetonitrile by OMDEX. Extraction efficiencies of OMDEX and conventional techniques were almost similar for SMPs. Thus the advantages of derivatisation–extraction over conventional sample preparation are that former has got better extraction efficiency for strongly adsorbing analytes and does not require evaporation of extracting solvent, which is essential in latter process to eliminate the protic solvents.

3.4. Method precision

Method precision of derivatisation–extraction was checked using acetonitrile as extraction solvent because best recoveries were obtained with it. Within- and between-day precision of OMDEX of NMPs and SMPs was tested on spiked (5 and 10 μg/g) soil. The overall relative standard deviations of the within-day repeatability ($n = 4$) and between-day reproducibility (five consecutive days, triplicate runs every day) were <3.3% and <4.6%, respectively. This demonstrates the repeatability of the method at the spiking concentrations generally given in the OPCW proficiency tests (OPTs).

3.5. Application of OMDEX method on soil sample of 16th official proficiency test

In the 16th proficiency test, one of the matrices was soil, which was fortified with precursors of nitrogen mustards.

Table 4
Recoveries of NMPs and SMPs from fortified soil with recommended procedure

Entry	Solvent	Recovery (%)					
		NMP1	NMP2	NMP3	SMP1	SMP2	SMP3
1	Methanol	30.2[a] ± 1.9	30.5[a] ± 1.7	20.7[a] ± 1.0	83.7 ± 1.7	94.2 ± 1.3	92.0 ± 2.0
2	Water	65.0 ± 2.8	66.1 ± 3.0	66.3 ± 2.5	82.3 ± 2.0	83.5 ± 1.2	92.2 ± 1.6

[a] Extracted with alkaline methanol (1% TEA).

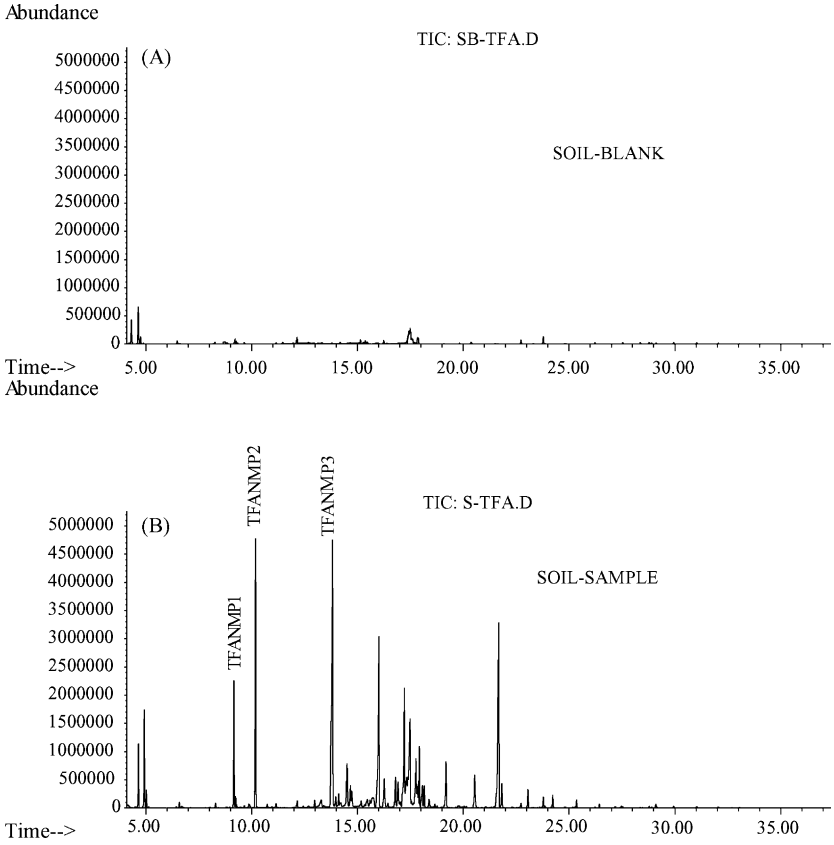

Fig. 4. Total ion chromatograms of (A) blank and (B) sample after on-matrix derivatisation–extraction of soil of 16th official proficiency test.

Having developed the on-matrix derivatisative–extraction method for NMPs, we tested it on the supplied sample. The sample (500 mg soil) was treated with TFAI followed by extraction with ethylacetate and heptane. The ethyl acetate and heptane were used as extracting solvent in this qualitative analysis because they did not dissolve the imidazole generated during derivatisation reaction; it showed relatively clean total ion chromatogram in GC–MS. The generated aliquot was analyzed by GC–MS in full scan mode, because in OPTs the identity of analytes is not known to the analyst and for unequivocal identification, the analysis is to be performed in full scan mode. Total ion chromatograms obtained for 'blank' (un-spiked) and 'sample' (spiked) soil after OMDEX are shown in Fig. 4. The TIC of blank is relatively clean than that of sample. It indicates that no spiked and background chemicals were present in blank. It is worth noticing that the trifluoroacetylated derivatives of NMPs were well resolved from background chemicals added in the sample to complicate the analysis. Trifluoroacetylated derivatives of all the NMPs were clearly detected and identified without any difficulty demonstrating the application of the method on an unknown sample. Thus, if this procedure is further optimized with different types of soils and background chemicals, it can be adopted for the off-site analysis of SMPs and NMPs used for the verification of CWC. This process of further optimization is in progress in our laboratory.

4. Conclusion

This study has dealt with the standardization of a technique known as derivatisation–extraction of precursors of nitrogen- and sulfur-mustards. NMPs and SMPs are important markers of vesicant class of CWAs, so their detection and identification is of vital importance from the verification point of view of CWC. The general protocol for their retrospective identification involves extraction, concentration and derivatisation, which is time-consuming and results in relatively lesser recoveries of some analytes from strongly adsorbing matrix like soil. Derivatisation preceding extraction converts these polar analytes into relatively non-polar compounds reducing the interaction with polar adsorbing surfaces. Subsequent extraction with suitable solvent recovers the derivatised analytes more efficiently. Trifluoroacetylation reactions with TFAI on spiked soil followed by extraction with organic solvents were optimized to recover the NMPs and SMPs. This technique was termed as on-matrix derivatisation–extraction. Selection of solvent for OMDEX technique was based on screening aprotic solvents of varying polarity for recovering

the NMPs and SMPs. The highest recoveries were obtained with acetonitrile, which further exhibited the best extraction efficiency for highly adsorptive NMP3. Comparison of recoveries of analytes by OMDEX and conventional extraction protocol was also made, which revealed that NMPs were better extracted with this new procedure and that SMPs too exhibited comparable recoveries. Parameters such as dynamic linearity range, repeatability and reproducibility were also determined. The applicability of the OMDEX technique was tested on 16th official proficiency test soil sample, where all the spiked precursors of nitrogen-mustards were detected.

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