DECONTAMINATION EFFICIENCY OF NERVE AGENT SOMAN (GD) WITH A NEW AMINO-ALCOHOLIC SOLUTION

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Soman (GD) it is known as one of the nerve agents which are the most toxic of the known chemical warfare agents (CWA), with a lethal dose of 1 to 10 mL on the skin, for humans.

The purpose of this paper is to test the decontamination efficiency of GD with a newly developed amino-alcoholic based decontamination solution, identify and quantify the GD decontamination products. The decontamination efficiency was checked by GC-MS/EI investigations after 2, 5, 7, 10, 15, 30, 60 min, 5 h and 24 h. The main degradation products were monitored and their concentration after decontamination was quantified. A GD degradation mechanism under the action of the amino-alcoholic solution was proposed.

Keywords: decontamination, gas chromatography, mass spectrometry, soman

1. Introduction

Soman (GD) it is one of the most toxic nerve agents known from chemical warfare agents (CWAs). A dose of 1 to 10 mL GD on the skin can be fatal within minutes for humans. It has an odor like camphor or rotting fruit. Nerve agents are chemically similar to organophosphorus pesticides and exert their effects by interfering with the normal function of the nervous system [1, 2].

Nerve agents have been often used in combat zones as tactical weapons and for terrorism during recent decades. In particular, nerve agents have not only

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fatal effects in acute phase of poisoning but also considerable long-term complications due to irreversible inhibition of acetylcholinesterase [3, 4]. Although all CWAs are banned by the Chemical Weapons Convention, several countries are still stockpiling chemical agents [5]. Therefore, effective decontamination methods must be prepared in order to protect people and important facilities from the effect of CWAs [6, 7]. Hydrolysis, oxidation, nucleophilic and electrophilic substitution [7] or photochemical reactions [8, 9] represent the most common degradation mechanisms

The novelty of this paper is to establish the decontamination efficiency of a real chemical warfare agent, GD, with a newly developed amino-alcoholic based decontamination solution and to identify and quantify the GD decontamination products. The decontamination efficiency was evaluated by Gas Chromatography - Mass Spectrometry / Electron Impact (GC-MS/EI) investigations after 2, 5, 7, 10, 15, 30, 60 min, 5 h and 24 h. The main degradation products were monitored and their concentration after decontamination was quantified. A GD mixture transformation mechanism under the action of the amino-alcoholic solution is proposed [10].

2. Experimental work

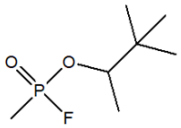
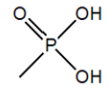
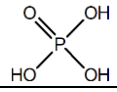
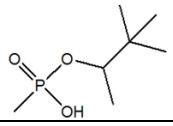
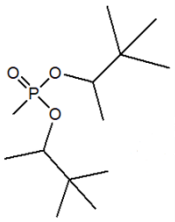
The first objective of this research was to research and develop a new decontamination solution (SD). The main active components of the solution are monoethanolamine, ethylcellosolve, NaOH 48%, isopropyl alcohol and sodium lauryl sulfate.

The second objective consist in testing SD`s decontamination efficiency against GD after several minutes to hours after toxic-decontaminant contact, monitoring the compounds resulting from decontamination actions and highlighting the degradation compounds resulting from the reactions between SD components and GD, by GC-MS/EI analyses. A GD purity test was performed, derivatizing 1 µL GD with 20 µL N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) within 1 mL dichloromethane (DCM), for 30 minutes at 60 °C. The following compounds and their concentrations were identified: O- pinacolyl methylfluorophosphonate (soman / GD – C1) 91 %, methylphosphonic acid 1.2 % (C2), phosphoric acid 0.04 % (C3), O-pinacolylmethylphosphonate 4.7 % (C4) and O-pinacolyl O-pinacolyl methylphosphonate 3 % (C5) (Table 1).

Two series of experiments were performed and the results were checked by GC-MS analyses. For both series, a 10 mL sample of SD was prepared, added to an amount of 33 µL GD mixture under stirring. The equivalent concentration of GD in SD is 3 µg / mL SD.

Table no. 1.

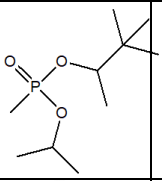
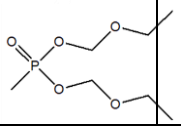
Compounds identified in the reference sample

Compound code	Compound name	Retention time (min.)	Chemical structure
C1	O-pinacolyl methylfluorophosphonate (GD)	8.58	
C2	Methylphosphonic acid - degradation product	10.18	
C3	Phosphoric acid - degradation product	12.28	
C4	O-Pinacolyl methylphosphonate - degradation product	12.57	
C5	O-Pinacolyl O-pinacolyl methylphosphonate - by-product from the synthesis of GD	15.03	

Samples were taken after 5 min, 10 min, 30 min, 60 min, 5 h and 24 h in the case of the first series, and after 2 min, 7 min, 15 min, 30 min, 60 min in the case of the second series and were prepared. 1 mL of the mixture was added over 2 mL DCM. The solution was dried over sodium sulfate to remove traces of existing water (SD containing 2% NaOH solution 48% in water) and filtered through a Sartorius 45 µm filter. 1 mL of the filtered solution is derivatized with 20 µL BSTFA for 30 min. at 60 °C.

Table no. 2

Decontamination products monitored in the decontamination process

Compound code	Name	Chemical structure	Molecular weight (g)	CAS	Retention time (min.)
C6	O-isopropyl, O-pinacolyl methylphosphonate		222	92411-67-1	12,26 Schedule 2.B.04
C7	methylphosphonic acid, di (2-ethoxyethyl) ester		240	6069-07-4	15,24 Schedule 2.B.04

The decontamination process takes place with formation of two compounds: O-isopropyl O-pinacolyl methylphosphonate (C6) and methylphosphonic acid, di(2-ethoxyethyl) ester (C7) (Table no. 2 above), both schedule 2.B.04. in Chemical Weapons Convention, identified by GC-MS/EI (Fig. 1 and Fig. 2).

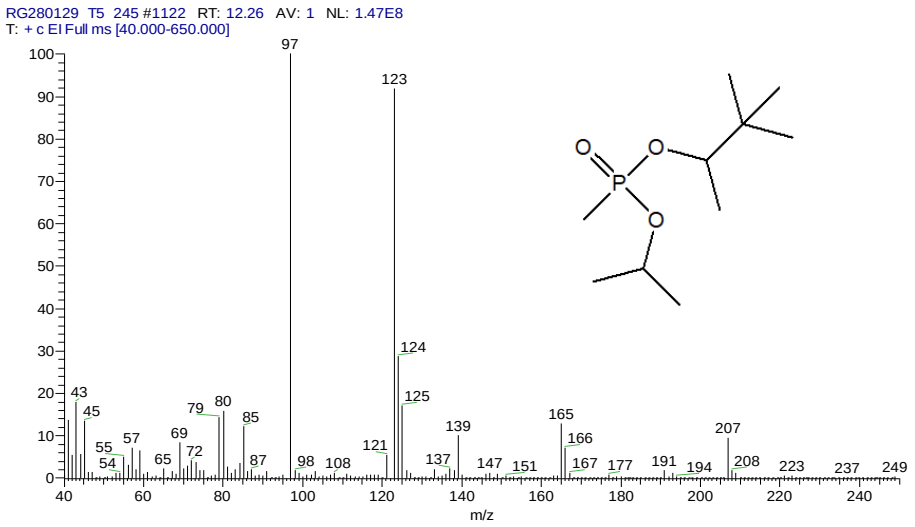


Fig. 1. EI mass spectrum of the compound O-isopropyl, O-pinacolyl methylphosphonate

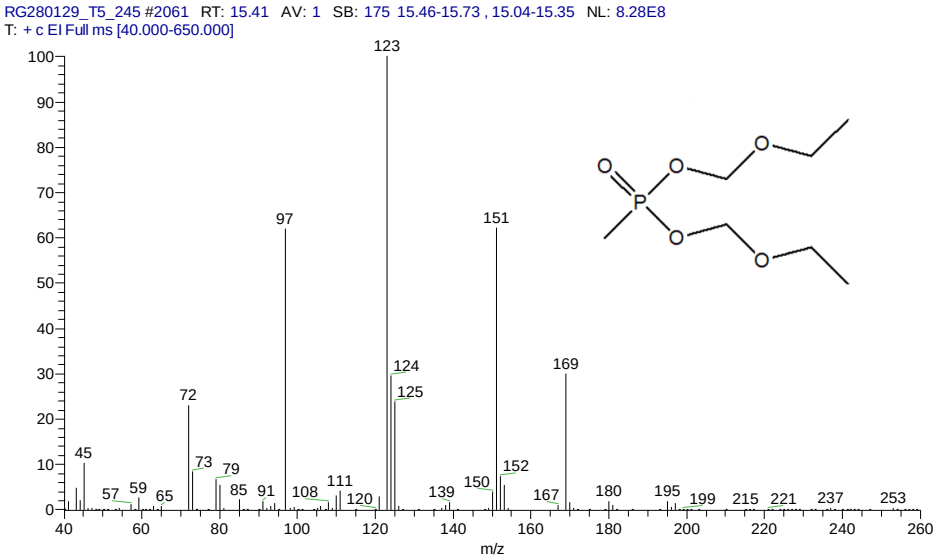


Fig. 3. EI mass spectrum of the compound methylphosphonic acid, di (2-ethoxyethyl) ester

3. Results and discussions

Tables 3 and 4 show the data obtained from the chromatograms after decontamination.

Table no. 3

Series 1 of experiments

Compound code	Exposure time (min)					
	5	10	30	60	5 h	24 h
SERIES I						
Area ($*10^6$)						
C1	390	357	153	143	-	-
C6	662	1698	1183	1275	1368	1231
C7	34045	36015	37094	40090	43624	44646
Amount of compound in decontamination solution (mg)						
C1	0.011	0.010	0.004	0.004	-	-
C6	0.0174	0.0447	0.0311	0.0336	0.0360	0.0324
C7	0.894	0.9466	0.9750	1.053	1.146	1.173
	% GD transformed into					
C6*	1.70	4.37	3.04	3.27	3.51	3.17
C7*	87.56	92.62	95.40	103.10	112.19	114.82
	% GD undecontaminated					
C1*	1.068	0.978	0.421	0.394	-	-
	GD decontamination efficiency (%)					
C1	98.93	99.02	99.57	99.60	100	100

* refers to C1

The remaining amount of GD (C1) was monitored, related to the peak area value in the reference GD solution (1 µg GD / mL DCM). It is observed in the case of series 1, the percentage of undecontaminated GD varying between 0% (5 h and 24 h) and 1.07 % (5 min), leading to a decontamination efficiency of 98.93 % to 100 % (Fig. 5). In the case of series 2, the percentage of undecontaminated GD varies between 0.39 % (1 h) and 1.11 % (2 min), Therefore, the decontamination efficiency varies between 98.89 % and 99.60 % (Fig. 6). Analyzing the results obtained in both series, a decontamination between 98.93 % and 100 % is observed (Fig. 7).

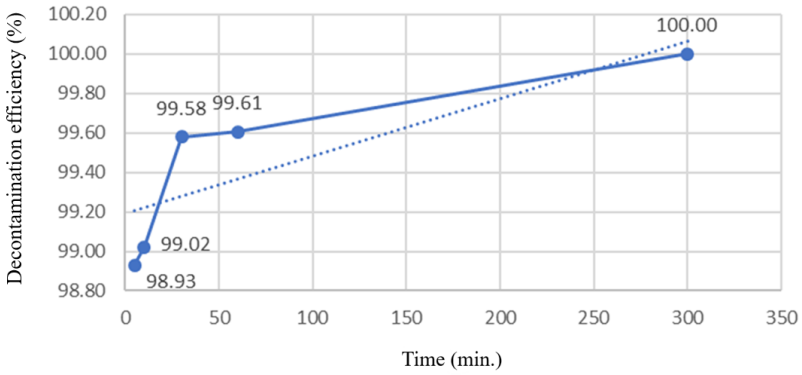


Fig. 5. GD decontamination efficiency as a function of time for Series 1 of tests

Table no. 4.

Series 2 experiments

Compound code	Exposure time (min)				
	2	7	15	30	60
SERIES II					
Area (*10^6)					
C1	406	359	300	153	143
C6	1186	1384	612	1165	1463
C7	36517	35826	38581	40505	43594
Amount of compound in decontamination solution (mg)					
C6	0.031	0.036	0.016	0.030	0.038
C7	0.96	0.94	1.01	1.06	1.15
	% GD transformed into				
C6*	3.05	3.56	1.57	3.00	3.76
C7*	93.91	92.13	99.22	104.17	112.11
	% GD undecontaminated				
C1*	1.112	0.984	0.822	0.42	0.39
	GD decontamination efficiency (%)				
C1	98.89	98.97	99.50	99.57	99.60

* refers to C1

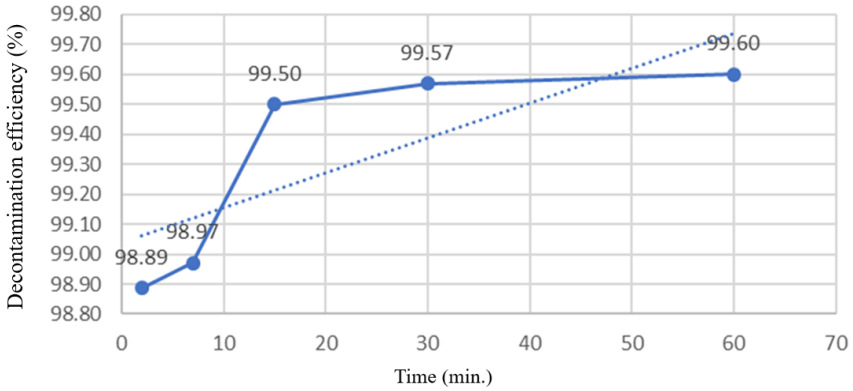


Fig. 6. GD decontamination efficiency as a function of time for Series 2 of tests

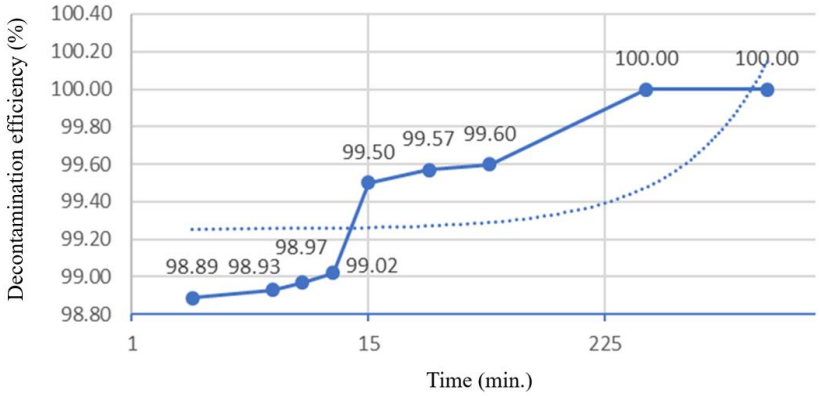


Fig. 7. GD decontamination efficiency as a function of time

The compounds O-isopropyl, O-1,2,2-pinacolyl methylphosphonate (C6) and methylphosphonic acid, (2-ethoxyethyl) ester (C7) show a nonlinear increase of concentration in the decontaminated samples. C6 can record a conversion ratio of 1.58 % and 3.76 %, and C7 reports 92 % to 114 % (Fig. 8).

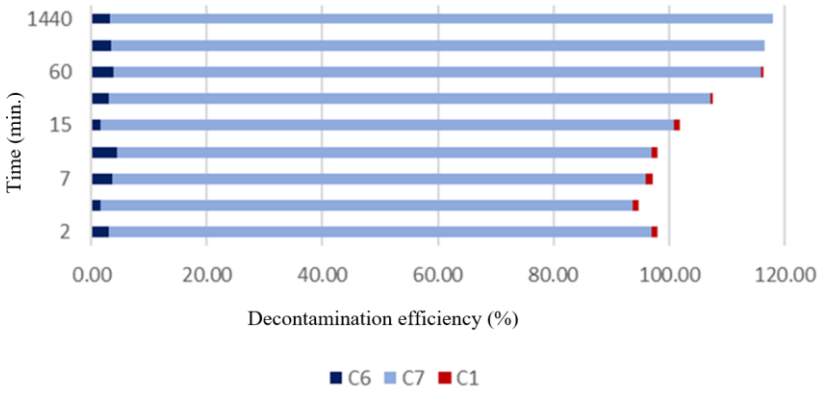


Fig. 8. Degree of conversion of the toxic into the decontamination products

The reason why the degree of transformation exceeds 100 % is due to the fact that GD was initially reported in the reference solution, but the initial solution contains 9 % other compounds that also react with the decontamination solution and lead to the same decontamination products, C6 and C7, as is it shown in the proposed mechanism of transformation (Fig. 9).

Considering the data obtained from chromatographic analyses, it is assumed that the isopropyl alcohol from SD reacts predominantly with pinacolyl methylphosphonate resulting O-isopropyl, O-pinacolyl methylphosphonate and the ethylcellosolve reacts very fast with GD resulting methylphosphonic acid, di(2-ethoxyethyl) ester. Methylphosphonic acid reacts preponderantly with ethylcellosolve resulting also methylphosphonic acid, di(2-ethoxyethyl).

Phosphoric acid was neglected due to it`s very low concentration prom the reference mixture. O-pinacolyl O-pinacolyl methylphosphonate, the GD synthesis by-product has no reaction with the SD, it`s concentration remaining constant. The following transformation mechanism is proposed:

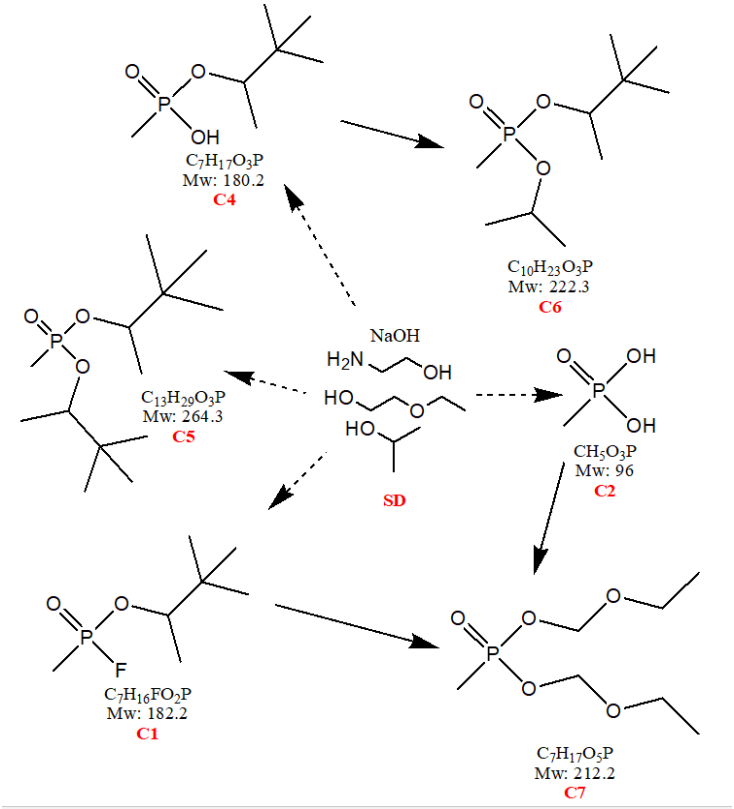


Fig. 9. The transformation mechanism of the toxic mixture containing 91% soman, under the action of the SD decontamination solution

4. Conclusions

Nerve agent GD it`s a highly toxic CWAs that must be decontaminated for the protection of the people and the important facilities. This paper work presented the results obtained from the process of GD decontamination with a newly developed amino-alcoholic decontamination solution. The following were highlighted:

A toxic mixture containing 91 % GD and 9 % GD degradation products and synthesis by-products was decontaminated with a decontamination solution based on monoethanolamine, ethylcellosolve, NaOH 48%, isopropyl alcohol and sodium lauryl sulfate.

The decontamination process takes place with formation of two compounds O-isopropyl, O-pinacolyl methylphosphonate (C6) and methylphosphonic acid, di(2-ethoxyethyl) ester (C7).

The decontamination process was checked by GC-MS/EI after 2, 5, 7, 10, 15, 30, 60 min, 5 h and 24 h, and the concentration of the decontamination products formed was quantified. The decontamination efficiency was between 98.93 % (after 2 min.) and 100 % (after 5 h).

A mechanism for decontamination of the toxic mixture containing 91 % GD with the present decontamination solution was proposed as follows: methylphosphonic acid and GD are transformed into methylphosphonic acid, di(2-ethoxyethyl) ester and pinacolylmethylphosphonate is converted to O-isopropyl, O-pinacolyl methylphosphonate. O-pinacolyl O-pinacolyl methylphosphonate, the GD synthesis by-product has no reaction with the SD, it`s concentration remaining constant.

Acknowledgements

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R E F E R E N C E S

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