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EVALUATION OF THE TEMPERATURE SENSITIVITY OF THE LACHRYMATORY IRRITANT 2-CHLOROBENZALMALONONITRILE BY DIFFERENTIAL SCANNING CALORIMETRY AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Mihail MUNTEANU*, Maria Daniela SANDU*, Cristiana EPURE*, Tudor-Viorel ȚIGĂNESCU**

***CBRN Defence and Ecology Research and Innovation Center, Bucharest, Romania
****"Ferdinand I" Military Technical Academy, Bucharest, Romania
mihail.munteanu@nbce.ro**

Abstract: *Pyrotechnic compositions are mixtures of several components which, when ignited, undergo energetic chemical reactions at a controlled rate to produce on-demand delay times, amounts of heat, noise, smoke, light or IR radiation. In general, pyrotechnic compositions are easily ignited, burn quickly and produce residues that are very hot. 2-Chlorbenzalmalononitrile (CS) belongs to the category of riot control agents and is used in various pyrotechnic tear gas compositions.*
The thermal characterization of tear pyrotechnic compositions is important for setting operating limits in the safety of the production process, storage, handling and even safe demilitarization.
In this sense, an experimental study was carried out to evaluate the behavior of CS at high temperatures, at different heating rates, by differential scanning calorimetry. Thermal changes were evaluated at a heating rate of 10, 20, 100 and 200°C/minute. The remaining residue was extracted in a suitable organic solvent and analyzed by gas chromatography coupled with mass spectrometry for the detection, identification and confirmation of the products formed during the controlled heating processes.

Keywords: 2-Chlorbenzalmalononitrile, thermal degradation, differential scanning, mass spectrometry, thermal stability

1. Introduction

According to document SAB-25/W.P.1 [1] of 27.03.2017 "Response to the Director-General's request to the Scientific Advisory Board to provide consideration on which Riot Control Agents (RCA) are subject to declaration under the Chemical Weapons Convention", issued by the Organization for Prohibition of Chemical Weapons (OPCW) Scientific Advisory Board (SAB), there are 17 substances that meet the definition of a riot control agent (RCA), as stated in Article II, paragraph 7 of the Convention. Article II, paragraph 7 of the Convention defines RCA as "any chemical substance not on the lists of the Convention which can rapidly produce sensory irritation or disabling physical effects in humans, effects which disappear shortly after exposure ceases".

2-Chlorobenzalmalononitrile, no. CAS 2698-41-1, military code CS, is the most common RCA, in its pure state it is a white solid powder with a pepper-like odor, melting at 93–95°C and boiling at 310-315°C. The CS is stable during storage and thermal action, and can be used in a mixture with fumigants and other aerosol production systems [2].

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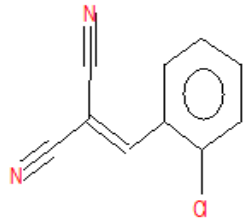


2-Chlorobenzalmalononitrile (CS)
CAS No. 2698-41-1
$C_{10}H_5ClN_2$; M = 188 g/mol

2. Methods and Tests

2.1. Determination of CS Purity by Gas Chromatography-Mass Spectrometry (GC/MS)

The irritant-lachrimatory substance, 2-Chlorbenzalmalononitrile used in the thermal sensitivity evaluation study, was synthesized in our own laboratory and characterized by gas chromatography coupled with mass spectrometry (GC/MS).

Equipment: GC-MS/MS Thermo Scientific Trace 1310 – TSQ 9000 chromatographic system

Operational parameters:

- Mobile phase flow rate: 1 ml/min helium;
- Sample injection mode: splitless, with solvent delay depending on the solvent used;
- Injection temperature: 250°C;
- GC column characteristics: TR 5MS/5% Phenyl 95% dimethylpolysiloxane:
  - length: 25-30 m;
  - inner diameter: di = 0.20 - 0.30 mm.
  - the standard thickness of the stationary phase film (0.25 - 0.33 µm);
- GC temperature program: 40°C (2 min.), 10°C/min., 280°C (10 min.)

2.2. Analysis by Differential Scanning Calorimetry (DSC)

Brief description of the differential scanning calorimetry (DSC) technique – allows the measurement of heat absorbed or released by a sample relative to a reference.

Differential scanning calorimetry, which measures heat capacity as a function of temperature, detects and monitors thermally induced conformational transitions and phase transitions. Depending on the transition that takes place, it can be with heat absorption (endothermic - for example melting, vaporization reactions) or with heat release (exothermic – for example decomposition reactions). The measuring principle of the DSC8000 Perkin Elmer equipment is through power compensated DSC, which transforms the temperature difference into caloric power, necessary to compensate the thermal balance between the sample and the reference.

Equipment and materials:

- Perkin Elmer DSC8000 differential scanning calorimeter;
- Sartorius high-precision analytical balance (±0.00001 g);
- melting temperature calibration standards;
- reusable stainless steel crucibles that withstand pressures of at least 130 bar.

Procedure: Similar amounts of CS (3.37 mg) were subjected to DSC analysis at a temperature program of 20-300°C with a heating rate of 10, 20, 100 and 200°C/minute. The purge gas was nitrogen of 99.9% purity; the purge gas pressure was 4 bars and the gas flow rate was 30 ml/min.

2.3. Analysis by GC/MS of the Residue Left after DSC Analysis

For the determination of the residue left in the crucible with the CS samples analyzed by DSC, a method was developed for the preparation, detection, identification and confirmation of the residue components by GC/MS analysis. Thus, the samples analyzed by DSC were subjected to the following extraction procedure:

- extraction of the DSC crucible containing the residue from the DSC analysis in a known volume of organic solvent (methylene chloride – DCM);
- ultrasonication of the vials with the crucible in the ultrasonic bath, for 2 hours, at a temperature of 20ºC;
- organic solvent filtration through Sartorius filter 0.45 µm;

- organic solvent collection in the 2 ml sample vial;
- GC/MS analysis.

For quantification, a control sample was also prepared (sample code CS_martor_DSC), a crucible containing the same amount of CS (3.37 mg) and a blank sample, the empty crucible inserted into the extraction solvent (code sample CS_blank_DSC).

3. Results and Discussion

3.1. DSC Analysis

The codification of the analyzed samples, corresponding to the work program applied with a heating rate of 10, 20, 100 and 200°C/minute, are as follows: CS_10DSC, CS_20DSC, CS_100DSC and CS_200DSC.

Figure 1 shows the DSC thermograms for the CS sample, analyzed with a temperature program with a rate of 10, 20, 100 and 200°C/minute.

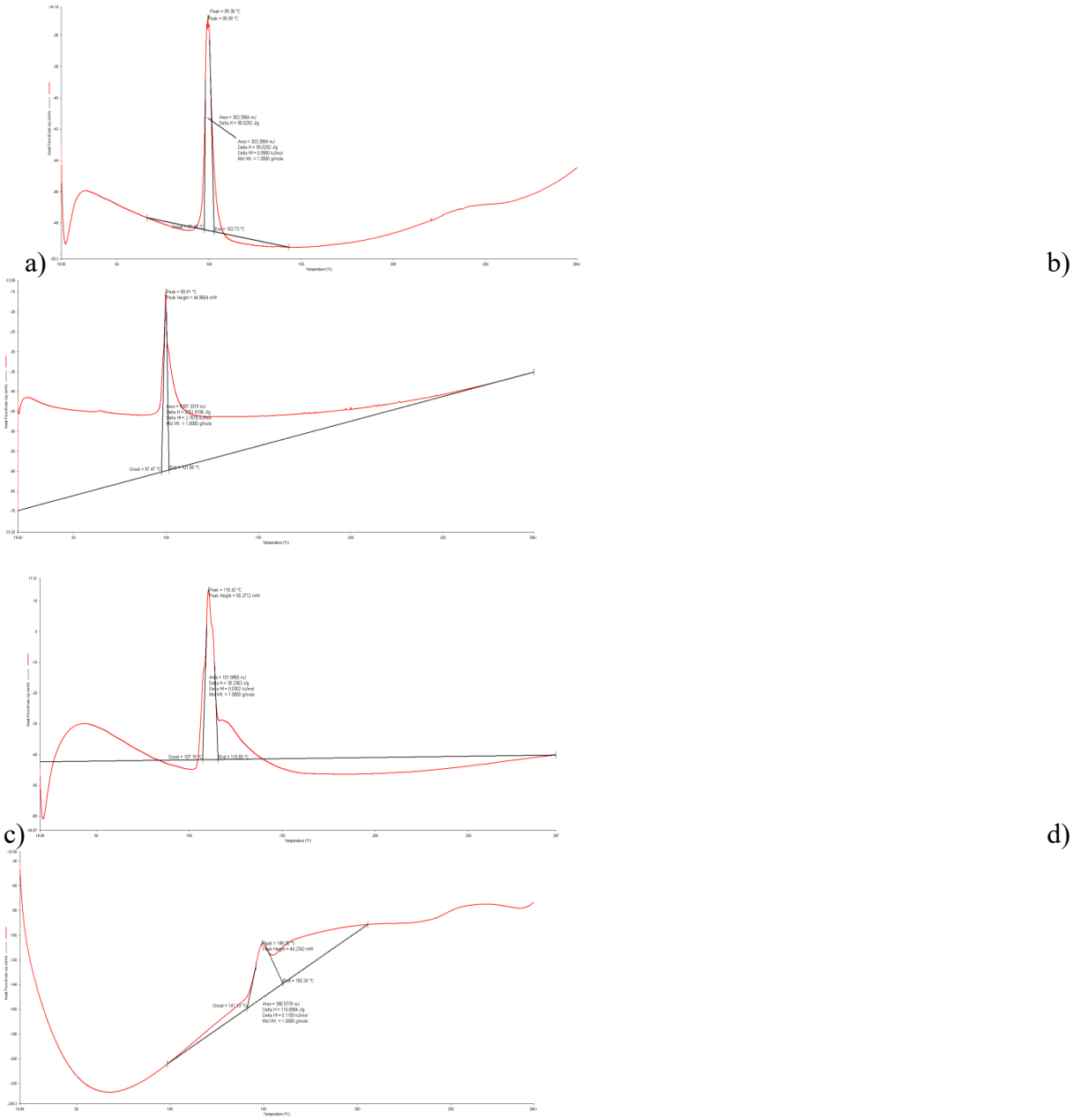


Figure 1: DSC thermogram for the CS sample, temperature program with: a) rate of 10°C/minute; b) 20°C/minute; c) 100°C/minute; d) 200°C/minute

The parameters measured in the DSC analysis, namely the type and temperature of the transition, the enthalpy of transition and the area of the peak of interest in the DSC thermogram, are presented in Table 1.

Table 1 Parameters monitored in DSC analysis

Sample code	Transition type	Transition temperature T_{tr} (°C)	Transition enthalpy $\Delta_{tr}H$ (J/g)	Peak area (mJ)
CS _10DSC	Melting	99,38	90,09	303,98
CS _20DSC		99,91	2761,81	9307,33
CS _100DSC		110,42	30,28	101,89
CS _200DSC		149,28	115,89	390,57

DSC thermal analysis shows an endothermic peak in the range of 99.38°C – 149.28°C and is associated with the melting temperature of CS, for different heating rates. In Figure 2, the 4 thermograms for the samples presented above are presented comparatively.

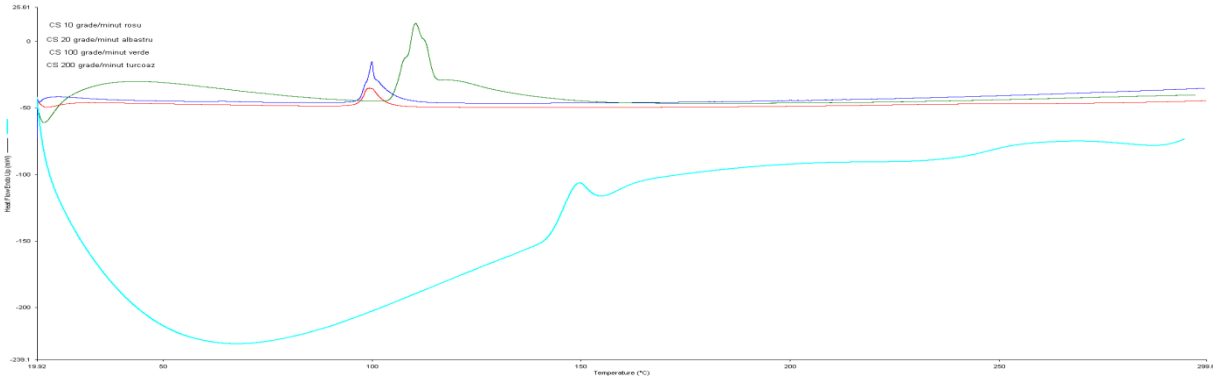


Figure 2: DSC thermograms for the CS samples analyzed at different heating rates. Temperature program 20-300°C; at a heating rate of 10°C/minute – T_{tr} 99.38°C, at 20°C/minute – T_{tr} 99.91°C, at 100°C/minute – T_{tr} 110.42°C and at 200°C/minute – T_{tr} 149. 28°C

3.2. Qualitative and Quantitative GC/MS Analysis of CS Samples Analyzed by DSC

The total ion chromatogram is shown in Figure 3. In addition to the compound of interest, CS, with a retention time of 15.78 minutes – C3, in insignificant amounts there is 2-chlorobenzaldehyde (9.75 minutes – C1), the raw material of the synthesis and 2 compounds from the CS family, namely 2-chlorobenzylmalononitrile (15.14 minutes – C2) and 2-(3-chlorobenzylidene)malononitrile (16.69 minutes – C4).

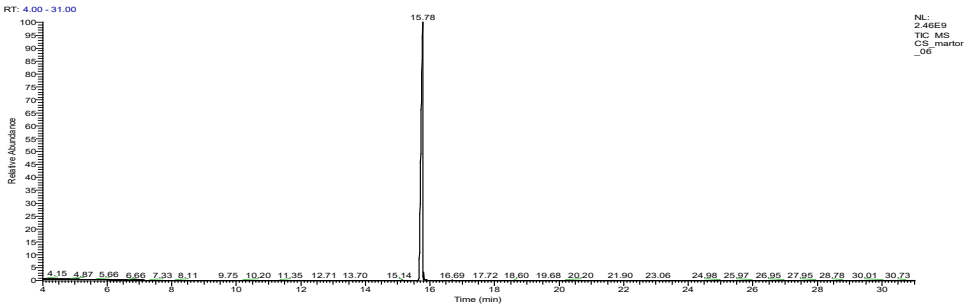


Figure 3: Total ion chromatogram for the sample containing the irritant-lacrimogenic substance CS

The components of CS synthesized in the laboratory, were detected and identified by GC/MS analysis and are presented in Table 2. According to the analyzes performed, CS has a purity of 99.8%, calculations performed and presented in Table 3. The identification of the irritant lachrymatory compound CS was done by gas chromatography coupled with mass spectrometry, by comparison with the spectrum from the NIST database, according to PS-02512C-14.00-001, ed.3, rev.1 - *Separation and identification of chemical compounds of military interest*, accredited procedure at national level (RENAR) and at international level (OPCW).

Table 2 Detected CS components and identified by GC/MS analysis

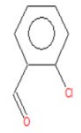
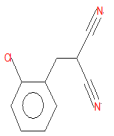
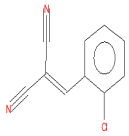
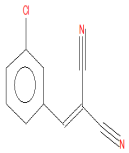
Compound name	**Retention time (minute)**	**Molecular formula**	**Chemical structure**
2-Chlorobenzaldehyde (C1)	9.75	C_7H_5ClO	
2-Chlorobenzylmalononitrile (C2)	15.14	$C_{10}H_7ClN_2$	
2-Chlorbenzalmalononitrile (CS-C3)	**15.78**	**$C_{10}H_5ClN_2$**	
2-(3-Chlorobenzylidene)malononitrile (C4)	16.69	$C_{10}H_5ClN_2$	

Table 3 Signals areas of CS components and the calculation of the percentage concentration

GC Area	**Component codification**			
	C1	**C2**	**C3**	**C4**
GC Area*10^6	5.2	9.4	**10593**	6,4
Procentual concentration (%)	0.048	0.088	**99.800**	0.064

The mass spectrum of the synthesized compound is shown in Figure 4, compared with the spectrum of the reference compound in the NIST database.

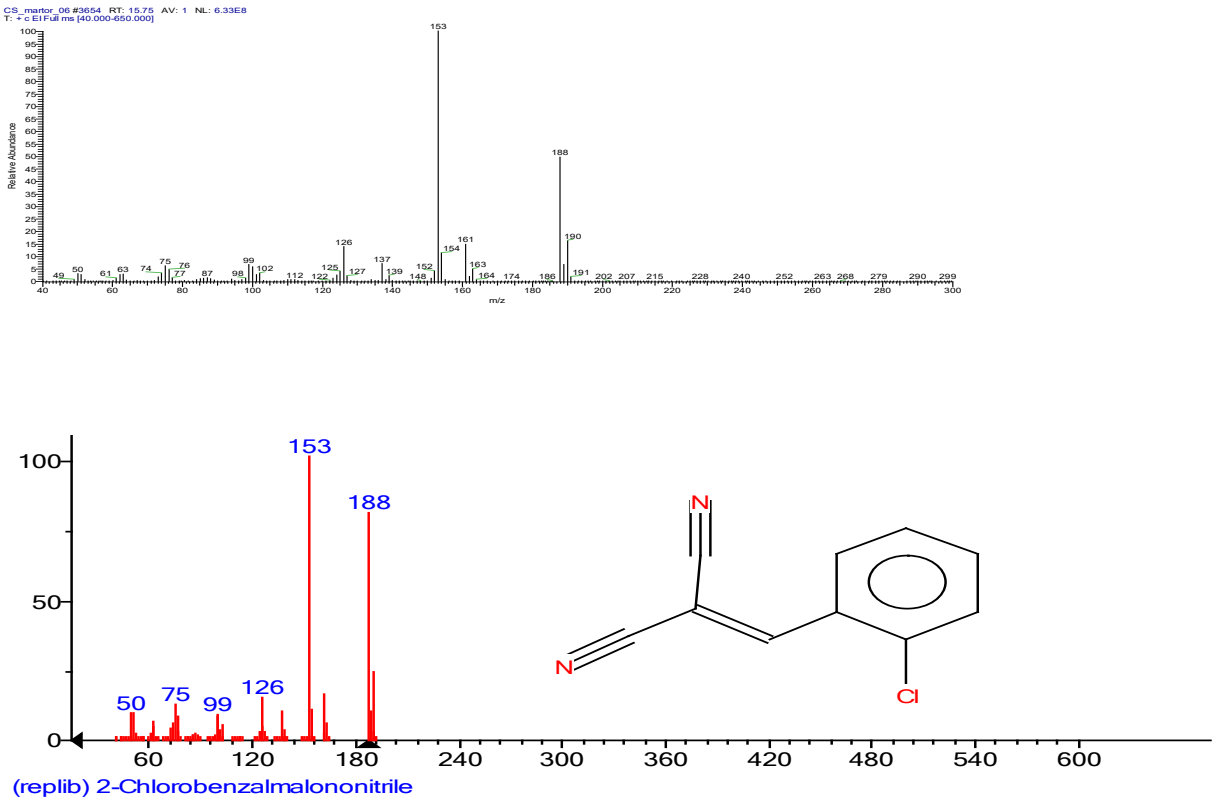
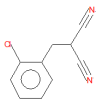
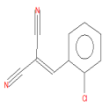
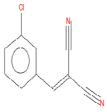


Figure 4: Mass spectrum of the synthesized compound (top), compared to the spectrum of the reference compound from the NIST database (bottom)

After GC/MS analysis of organic extracts of CS samples subjected to a DSC heating and analysis program, compounds identified and confirmed by mass spectra from the NIST database are shown in Table 4.

Table 4 Components of organic extracts after DSC analysis at different heating rates

Chemical name	Molecular formula	Chemical structure	M (g/mol)	CAS No.	Chemical code	Retention time (min.)
2-Chlorobenzaldehyde	C_7H_5ClO		140	89-98-5	C1	9.75
2-Chlorobenzylmalononitrile (C2) (dihydro CS)	$C_{10}H_7ClN_2$		190	40915-55-7	C2	15.14
2-Chlorbenzalmalononitrile (CS)	$C_{10}H_5ClN_2$		188	2698-41-1	C3	15.74
2-(3-Chlorobenzylidene)malononitrile	$C_{10}H_5ClN_2$		188	2972-73-8	C4	16.69

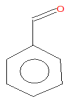
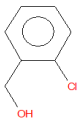
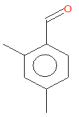
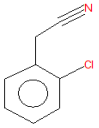
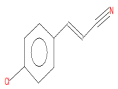
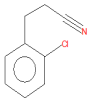
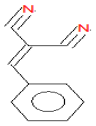
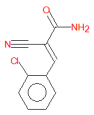
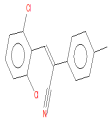
Benzaldehyde	C_7H_6O		106	100-52-7	C5	7.16
o-Chlorobenzonitrile	C_7H_4ClN		137	873-32-5	C6	10.57
2-Chlorobenzyl alcohol	C_7H_7ClO		142	17849-38-2	C7	11.17
2,4-Dimethylbenzaldehyde	$C_9H_{10}O$		134	15764-16-6	C8	11.23
2-Chlorobenzyl cyanides	C_8H_6ClN		151	2856-63-5	C9	12.24
p-Chlorocinnamonitrile	C_9H_6ClN		163	28446-72-2	C10	13.53
2-Chlorohydrocinnamonitrile	C_9H_8ClN		165	7315-17-5	C11	13.73
Benzylidenemalonodinitrile	$C_{10}H_6N_2$		154	2700-22-3	C12	14.45
O-Chloro-o-cyano-Cinnamamide	$C_{10}H_7ClN_2O$		206	3533-10-6	C13	19.24
3-(2,6-Dichloro-phenyl)-2-p-tolyl-acrylonitrile	$C_{16}H_{11}Cl_2N$		287	-	C14	23.06

Table 5 shows the percentage concentrations of the compounds identified and distributed in each analyzed sample.

Table 5 Percentage distribution of compounds identified in the samples analyzed by DSC

Sample code	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**	**Total %**
CSmartor	0.05	0.09	**99.80**	0.06	-	-	-	-	-	-	-	-	-	-	100
CS_10DSC	2.48	8.23	**85.73**	0.08	0.50	0.0600	0.03	0.05	0.02	0.380	0.57	1.65	0.1500	0.070	100
CS_20DSC	0.262	0.357	**99.25**	0.09	-	0.0070	-	-	-	0.004	-	-	0,0260	0.044	100
CS_100DSC	0.134	0.21	**99.55**	0.086	-	0.0033	-	-	-	-	-	-	0,0097	0.007	100
CS_200DSC	0.043	0.241	**99.65**	0.064	-	-	-	-	-	-	-	-	-	-	100

The appearance of the chromatographic peak corresponding to 2-chlorobenzaldehyde (compound C1) indicates a hydrolysis of CS. At a heating rate of 10°C/min. an increase in the content of C1 in the sample is observed, from 0.05 to 2.48% and a decrease in the content of CS (compound C3), from 99.80 to 85.73%.

Some of the compounds of interest are shown in Figure 5-7, on different areas of GC/MS analysis.

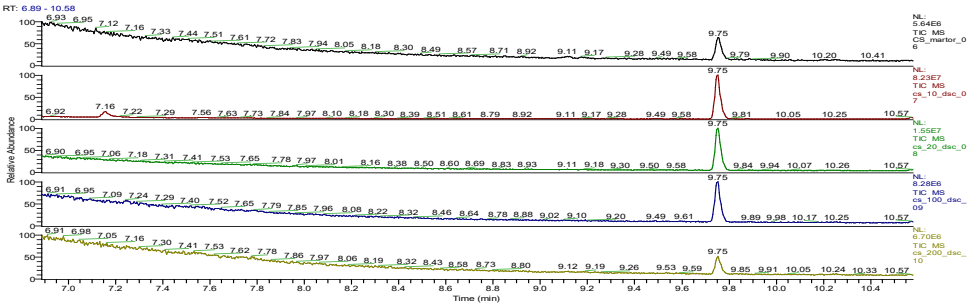


Figure 5: Total ion chromatogram for control CS sample and CS samples subjected to DSC analysis at different heating rates and extracted in methylene chloride (range 7.00 – 10.50 minutes). At retention time 9.75 minutes is 2-chlorobenzaldehyde (compound code C1) and at 7.16 minutes is benzaldehyde (compound code C5)

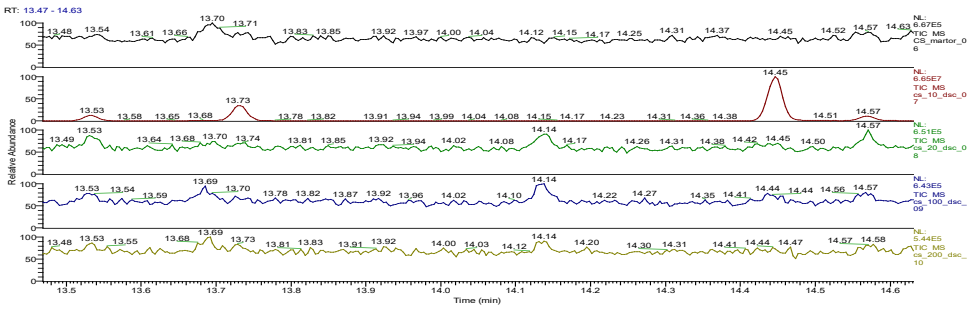


Figure 6: Total ion chromatogram for blank CS sample and CS samples subjected to DSC analysis at different heating rates and extracted in methylene chloride (range 13.50 – 14.60 minutes). Products of interest C10 (13.53 minutes), C11 (13.73 minutes) and C12 (14.45 minutes) are found

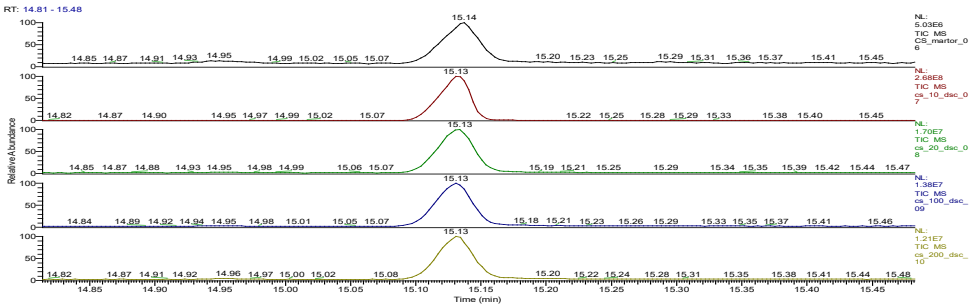


Figure 7: Total ion chromatogram for blank CS sample and CS samples subjected to DSC analysis at different heating rates and extracted in methylene chloride (range 14.85 – 15.45 minutes). At retention time 15.14 minutes is compound C2

Table 6 shows the mass concentration of CS found after GC/MS analyses, for the samples analyzed by DSC, at different heating rates of the samples.

Table 6 CS mass concentration for DSC analyzed samples at different heating rates

Sample code	Mass concentration CS (mg)	
	(µg CS/ml extraction solvent)	(µg CS/10 ml solvent/1000) (mg)
CSmartor_DSC	337.00	**3.370**
CS_10DSC	154.33	**1.543**
CS_20DSC	310.94	**3.109**
CS_100DSC	310.88	**3.108**
CS_200DSC	303.62	**3.036**

4. Possible Thermal Degradation Mechanism of the Irritant-Lachrimatory Substance, 2-Chlorbenzalmalononitrile

Figure 8 shows a possible mechanism that can occur during a slow thermal degradation of the CS (sample code CS_10DSC). The main thermal degradation products are C2 (dihydro CS) in a proportion of 8.23%, C1 (2-chlorobenzaldehyde) with 2.48% and C12 (benzylidenemalonodinitrile) with 1.65%.

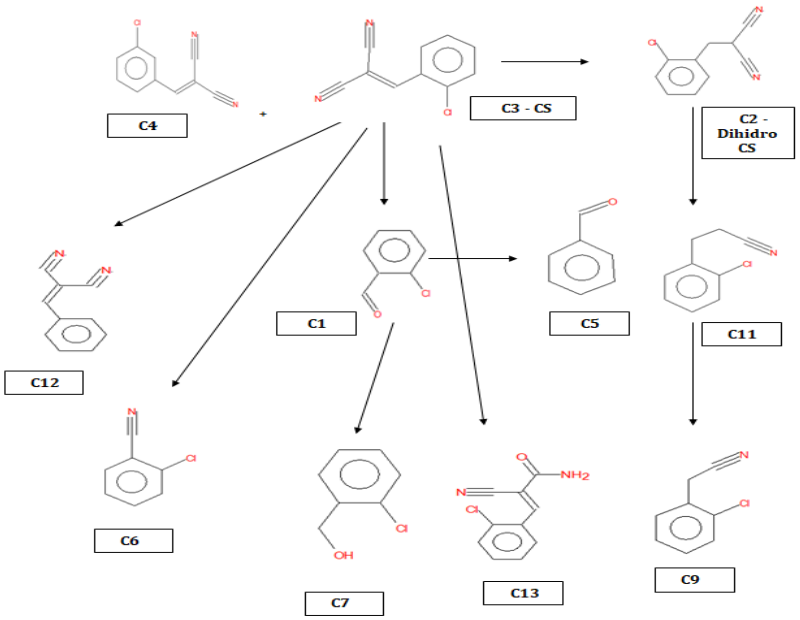


Figure 8: Thermal degradation products of CS (sample code CS_10DSC). In a considerable proportion the compounds C1, C2 and C12 are formed

5. Conclusions

The recovery degree of CS decreases in the CS_10DSC sample from 3.37 mg (control sample) to 1.54 mg, due to the transition phenomena that take place (crystallization, melting, sublimation, decomposition), upon a slow heating of the sample in the DSC crucible. In this sample, 10 degradation products were observed, species with lower molecular masses and potentially adverse effects, which were formed by the loss of cyan or chlorine fragments from the CS molecule or by a rearrangement of the molecule. In the case of sample CS_20DSC, the finding in a small proportion of the compound 2-Chlorohydrocinnamonitrile

(C11 - 0.57%) leads to the conclusion that there was a considerable release of hydrocyanic acid (HCN), coming from the compound C2 (dihydro CS – 8.23%). However, in all samples analyzed, the dominant compound was the irritant-lachrimatory substance CS. For the coded samples CS_20DSC and CS_100DSC, the degradation products occupy only an insignificant amount, well below 0.1% and for the sample CS_200DSC only a slight increase of the CS dihydro compound is observed, the CS content being 99.65%.

The findings of these studies have implications not only for health risk assessment but also for the development of safer thermal devices that use tear agents. These results suggest the need to develop CS devices that develop low temperatures, thus resulting in a low probability of generating toxic CS degradation products.

Acknowledgements

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References List

[1] OPCW SAB-25/WP.1 /27 March 2017, "*Response to the Director-General's request to the Scientific Advisory Board to provide consideration on which Riot Control Agents (RCA) are subject to declaration under the Chemical Weapons Convention",* OPCW Scientific Advisory Board, March 2017.

[2] Chemistries of Chemical Warfare Agents, Terry J. Henderson, Ilona Petrikovics, Petr Kikilo, Andrew L. Ternay Jr., Harry Salem, 2019, ISBN 9781498769235.