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SCREENING OF CHEMICAL WARFARE AGENTS AND THEIR DEGRADATION PRODUCTS

SKRINING OTROVNIH HEMIJSKIH SUPSTANCI I NJIHOVIH DEGRADACIONIH PRODUKATA

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Ključne reči
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Abstract

Chemical warfare agents (CWA) have been used as a chemical weapon against military personnel, as well as in terrorist activities. Because CWA can cause serious injury or death, it is very important to detect them in a short period of time. Identification of compound which was used in attack is the major task in applying of antidotes therapy and treating of poisoned.

Detector for screening can give structural information about chemical class of CWA. For identification of single compound, only selective detector can be used. The most used selective detector is mass spectrometer. It can be used to screen groups of chemicals based on characteristic ions. Different types of samples can be analyzed by gas chromatography with mass spectrometry (GC/MS). GC/MS in scan mode is used to screen all chemicals of interest. By using different software, combined with a proper target library, the acquired data can be analysed manually or automatically and chemicals of interest can be identified. This screening technique is based on one or more properties of CWA which are separated from irrelevant compounds.

GC/MS enables simultaneous identification not only single compounds from different chemical groups, but also its degradation products which is important in confirmation of CWA use.

INTRODUCTION

Chemical warfare agents (CWA) are toxic chemicals that can be used as chemical weapons (chocking, blister, blood, nerve agents). They are divided into three groups:

1. Toxic chemicals that have been used as chemical weapons in the past and/or have very few or no peaceful uses (Schedule 1),

2. Chemicals which are primarily precursors to Schedule 1 (most of them have some industrial uses) (Schedule 2),

3. Chemicals which are produced commercially in large quantities; they were used as chemical warfare agents in some cases and can be precursors to Schedule 1 or 2 chemicals (Schedule 3).[1]

CWA have very high toxicity. Surviving in case of applying CWA depends on their fast detection. Detection of CWA is important step before treating of poisoned people. It is very important to detect them in a short period of time.

Identification of compound which was used in attack is the major task in applying of antidotes therapy and treating of poisoned.

Detectors in analysis of CWA

Different types of detector can be used for CWA detection. Ideal detector has to be constructed to detect CWA in short period of time and to has high sensitivity (to detect low concentration of CWA which may have influence on the health). Also, it has to be easy for operating and producing data.[2-3]

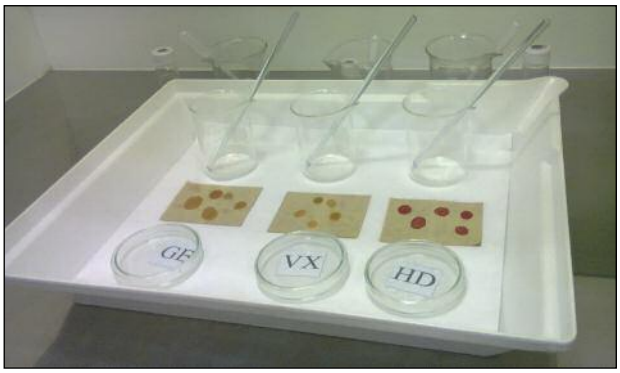
One of the most used detectors for screening of chemicals from the group of nerve (G) and mustard (H) agents is CAM (Chemical Agent Monitor) detector.

***Picture 1**. Chemical Agent Monitor (CAM Detector)*

CAM can detect only presence of G (soman, sarin, tabun) or H agents in the air, but it can not identify chemical structure of CWA. It is uses for screening of CWA. CAM detector is useful for detection of CWA in both field and laboratory conditions.

Simple detection and differentiation between three groups of CWA (G, V and H) in liquid form can be done by using identification papers CALID/DP3. Different chemicals will provide different colors on papers:

- green color – V agents
- yellow color – G agents
- purple color – luisite (L1) and mustard (H)



***Picture 2**. Indicator papers CALID/DP3*

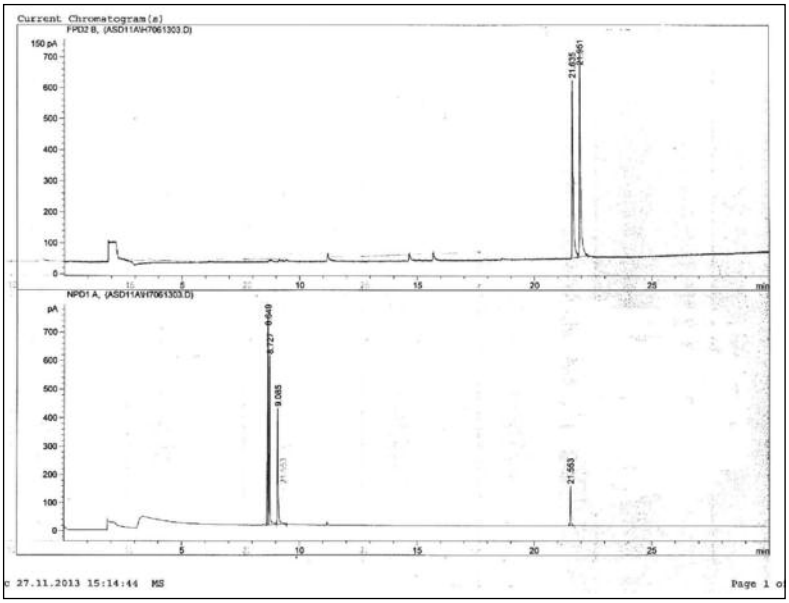
Screening of CWA in laboratory conditions

Screening of CWA in stationary laboratory uses different chromatographic and spectroscopic techniques such as gas and liquid chromatography with different detectors, infra red (IR) spectroscopy and nuclear magnetic resonance (NMR). It can enable reliable analysis to separate, detect and identify relevant from irrelevant chemicals.[1,4-7]

Screening has to be combination of various techniques. It can be non-targeted and targeted.

Non-targeted screening is general method for searching chemicals with similar structure, requires confirmation by other methods. The most used method for this type of screening is gas chromatography with selective nitrogen-phosphorus or flame-photometric detectors (GC-NPD, FPD). It can detect compounds with nitrogen or phosphorus (NPD) or compounds with phosphorus (P) and sulfur (S) (FPD). Non-targeted screening is first step in analysis of CWA, because the most of them contain N, P or S.

Targeted screening is method for identification of individual chemicals (GC-EI-MS).[1,8]



***Picture 3.** Chromatogram of the sample after analysis on FPD (on the top) and NPD (on the bottom)*

Mass spectrometric detector can be used as an universal detector when all chemicals are detected in full scan mode using electron impact ionization. It also can be selective detector for detection target chemicals in selective ion monitoring mode.[1,8]

Gass chromatography with mass spectrometry (GC/MS) provide information about chemical structure and molecular weight of CWA and degradation products. The advantage of this method is very good sensitivity and reliability. Thanks to different computer libraries it enables identification of not just unknown CWA, but their degradation products also.

GC/MS can be applied for screening of chemicals with or without N, P or S. It uses electron (EI) or chemical ionization (CI). EI always produces fragment ions. Mass spectrum of one compound is always the same under the same condition and can be identified by using libraries. CI give information about molecular weight.

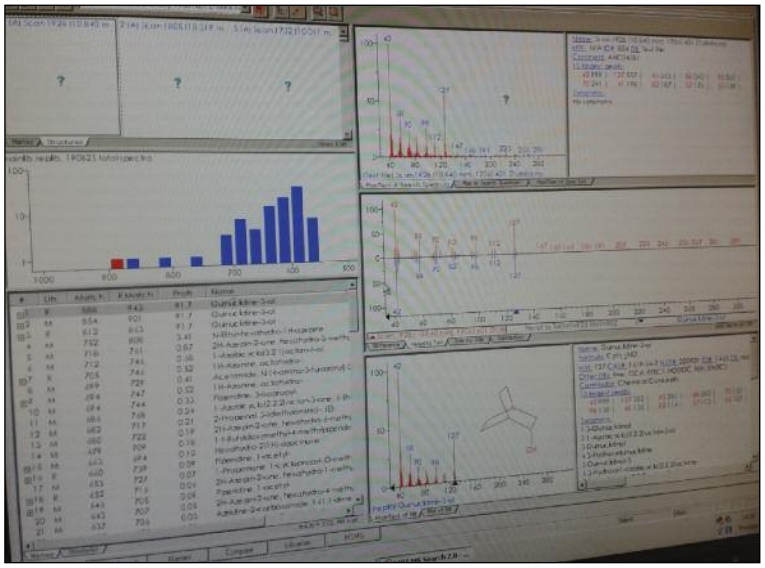
***Picture 4**: Gas chromatograph with mass spectrometric detector*

In mass spectrometry chemicals of interest are ionized and produced ions which are analyzed according to their mass-to-charge ratios (m/z).

Spectral interpretation and identification of chemicals is very complex task. It required very good knowledge of mass spectrometry, chemical properties and fragmentation of

organic compound, as well experience in that kind of analyses.

Regardless, identification of CWA and their degradation products based on their mass spectra in full scan mode is very reliable. It is performing by searching for ions (molecular or fragment) typical for the target chemicals. Gotten spectrum is compare with library spectrum (NIST, OCAD, Wiley, etc) or with spectrum of reference standard.



Picture 5: *Identification of unknown compound using NIST library*

Using of computer software for automatic data processing such as AMDIS (**A**utomated **M**ass Spectral **D**econvolution and **I**dentification **S**ystem) helps in identification of unknown CWA or its degradation products. This software can analized every peak in chromatogram, compare it with computer library and provide identification with a certain probability.

Identification of unknown compound after automatic and maual analysis as well as comparison of its mass spectrum with mass spectrum of analytical standard performed on that way is unambiguous.

CONCLUSION

Screening of CWA and their degradation products is very complex task. It uses diferent types of selective detectors. Owing to its specificity, selectivity and sensitivity, gas chromatography with mass spectrometry is powerful tool in confirmation and identification of CWA and degradation products in different samples after screening by GC/FID and NPD. Using different databases, as well as different software, mass spectrometry enables identification of traces of CWA and their degradation products in samples.

Sažetak

Otrovne hemijske supstance (bojni otrovi BOt) su korišćene kao hemijsko oružje kako protiv vojske, tako i u terorističkim napadima. Pošto mogu da izazovu ozbiljne ozlede ili smrt, veoma je važno detektovati ih u kratkom vremenskom periodu. Identifikacija jedinjenja koja su korišćena u napadu je važan zadatak zbog primene antidotske terapije i lečenja otrovanih. Detektori koji se koriste za skrining mogu dati informaciju o strukturi hemijske grupe BOt. Za identifikaciju pojedinačne komponente mogu se koristiti samo selektivni detektori. Maseni spektrometar je najviše korišćen selektivni detektor. Može se koristiti u skriningu grupe hemikalija na osnovu karakterističnih jona. Različite vrste uzoraka mogu se analizirati gasnom hromatografijom sa masenom spektrometrijom (GC/MS). GC/MS u skan modu se koristi u skriningu svih značajnih hemikalija. Korišćenjem različitih softvera u kombinaciji sa odgovarajućim bibliotekama, dobijeni podaci se mogu analizirati ručno ili automatski i na taj način identifikovati hemikalije od interesa. Ova skrining tehnika se bazira na jednom ili više svojstava BOt koji su razdvojeni od irelevantnih komponenata.

GC/MS omogućava istovremenu identifikaciju ne samo pojedinačnih komponenata koje pripadaju različitim hemijskim grupama, već i identifikaciju njihovih degradacionih produkata koji su značajni za potvrdu korišćenja BOt.

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